DEVELOPMENT AND APPLICATION OF TECHNICAL AND ECONOMIC STRATEGIES IN UPGRADING HEAVY OIL: THE CASE OF IRAN

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ABSTRACT

Nowadays, due to the increasing demand for energy at an alarming rate, the alternative resources of energy are being explored to compensate the depleting conventional energy resources. One such alternative, if the upgrading processes are effectively managed, could be heavy crude oil.

Iran is endowed with large resources of both conventional and unconventional Oil. However Due to the decrease in the conventional resources in Iran, the National Iranian Oil Company (NIOC) has been compelled to resort to the unconventional oil resources.

However, the transition to heavier and sourer oil resources results in some technical, economic and environmental challenges for the downstream refining industry in Iran.

These challenges require investing in new refinery technologies or/and a better crude feedstock to improve the quality of the downstream products. The best approach to curb major modifications for the current refineries is to upgrade heavy oil prior to its entrance to the refineries.

Carrying out this treatment under optimum reaction conditions would be economically attractive to Iranian National Oil Company.

This thesis discusses the development and application of technical and economical strategies to achieve an optimum solution for upgrading SOROOSH heavy oil. the first step was, to develop an experimental study based on the three most important variables for the hydro-treatment process and apply the ANN (Artificial Neural Network) system to predict the results. We identified a set of possible conditions to achieve the required feed specification for refineries in Iran i.e. sulphur and metals less than 1.6 %wt. and 100wppm respectively.

In the second step, based on the objective model, the Nonlinear Programming (NLP) models for processing conditions were carried out which included several types of logic models to demonstrate the combination of three main variables, HSD/ HDM and utilities.

Using MATLAB and SIMULINK software to simulate systematic models, the possible conditions (Temperature, Pressure and Liquid Hourly Space Velocity (LHSV)) for the desired HDS and HDM in the upgrading process of SOROOSH heavy oil were determined.

Finally, all the economical functions and the parameters were fed to the indigenous software developed at Amirkabir University of Technology (AUT). To estimate the best conditions from an economical point of view for a 50,000 BPSD from SOROOSH crude oil.

The results obtained from the simulation and the economic analysis; revealed suitable commercialization conditions under which an effective pathway to upgrade SOROOSH heavy oil, could potentially be provided with less capital cost.

This thesis has proven the practicality of the proposed model as an efficient tool for planning the upgrading of SOROOSH's heavy oil process from the technical and economical points of view and could open new markets for Iran and as a result increase the national revenue.

ABSTRAK

Dewasa kini, sumber tenaga alternatif dikaji untuk menggantikan sumber tenaga konvensional ekoran peningkatan pemintaan terhadap penggunaan sumber tenaga yang tinggi. "Minyak berat" boleh dianggap sebagai salah satu sumber alternatif selagi proses menaik taraf diuruskan dengan berkesan.

Iran dikurniakandengansumberminyakkonvensionaldanminyakbukankonvensional yang banyak.NIOC (National Iran Oil Company) perlu memenuhi apa yang dikenali sebagai spesifikasi sulfur ultra rendah yang digunakan di seluruh dunia berikutan penurunansumberkonvensional dankuasaberalih kepadatakungantidak konvensionalsebagaisumberalternatif. Oleh itu komposisi bahan yang dihantar ke kilang penapis telah menjadi lebih berat untuk hampir kesemua kes, dan ia tidak dapat diproses tanpa perubahan drastik, iaitu rombakan oleh tumbuh-tumbuhan atau pemasangan unit baru yang berkemampuan untuk mengendalikan bahan baru. Salah satu pendekatanyang terbaikuntuk mengelakkanpengubahsuaianutamakilang penapisialah menaik tarafpetroleumberatsebelum memasukiruang penyulingan. Di Iran, jika proses ini diaplikasikan secara ekonomi untuk lebihan "minyak berat", ia akan menjadi mudah untuk "minyak berat" yang lain.

Oleh hal yang demikian, tesis ini adalah untuk mengkaji sama ada menaik taraf "minyak berat" boleh membawa kepada pasaran baru dan meningkatkan pendapatan kepada negara Iran.

Oleh itu, dalam kajian ini, strategi yang paling sesuai untuk menaik taraf "minyak berat" di Iran telah dihasilkan untuk mencari strategi yang sesuai, di mana kemudiannya dibina kilang perintis dibina berdasarkan strategi terpilih dan pendekatan pengoptimuman multi-objektif telah dibangunkan untuk diskrinkan dan menetapkan syarat optimum. Akhir sekali, laluan optimum dinilai berdasarkan kepada kos kecekapan yang minimum dalam menggantikan masa lalu.

Sumbangan utama dalam kajian ini adalah untuk mencari parameter optimum yang boleh membawa kepada kos operasi yang minimum dan dapat memaksimumkan kecekapan dalam menaiktaraf "minyak berat" di Iran.

ACKNOWLEDGEMENTS

DEDICATION

This Thesis is dedicated to the memory of my revered

MOTHER

Who emotionally supported my studies during my BSc. and MSc.

She would have been very keen to have seen my Doctorate.

Peace be upon her

During my studies at University of Malaya and the fieldwork in Iran, I became indebted to a number of people whom I wish to acknowledge.

First of all, I would like to express my gratitude to my supervisor, Professor Dr. Hamdi, for his constant support, continuous encouragement and discerning comments during the elaboration of this thesis. I feel the virtues of this thesis reflect his comprehensive criticism and guidance. Further, I would like to thank Dr. AmirNaser Akhavan, my associate supervisor, for his assistance and critical comments during the earlier and final stages of this study. Without his constructive advice and guidance this would not have been completed. Thanks also go to the assistance staff of Prof Hamdi office and Library University of Malaya.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	Annual (Year)
AACE	Association for the Advancement of Cost Engineering
AGO	Atmospheric Gas Oil
ANN	Arterial Neural Network
ANOVA	Analysis Of Variance
API	American Petroleum Institute
ARAMIS	Advanced Refining Applicative Model for Integrated Studies
ARDS	Atmospheric Residue Desulfurization
AUT	AmirKabir University of Technology
bbl.	Barrel
BPSD	Barrel Per Stream Day
CAPEX	Capital Expenditure
CO_2	Carbon Dioxide
cSt:	Centistokes
DAO	Deasphalted Oil
DC	Delayed Coking
EST	Eni Slurry Technology
FC	Fluid Coking
FCC	Fluid Catalytic Cracking
HCK	Hydrocracking
HDA	Hydro-dearomatization
HDCCR	Conradson Carbon Removal
HDN	Hydro-denitrogenation
HDO	Hydro-deoxygenation

HDS	Hydro-desulfurization
HDT	Hydro-treating
HGO	Heavy Gas Oil
HPS	High Pressure Separator
HYCAR	Hydro-visbreaking Process
HYCON	Shell's Bunker type reactor
HYD	Hydrogenation
IRR	Internal Rate of Return
kbbl	thousand barrels
KOH	Potassium Hydroxide
LGO	Light Gas Oil
LL	Upper Level condition
LPG	Liquefied Petroleum Gas
LSFO	Low Sulphur Fuel Oil
MAE	Minimum/ Maximum Absolute Error
MBtu	Millions of British thermal unit
Mild HCk	Mild Hydrocracker
MSE	Mean Squared Error
MTBE	Methyl Tert-Butyl Ether
NPV	Net Present Value
OOIP	Original Oil In Place
PNA	Paraffins, Naphthenes, and Aromatics
POT	Pay Out Time
RFCC	Residuum Fluid Catalytic Cracking
RIPI	Research Institute of Petroleum Industry
RMSE	Root Means Squared Error

SARA	Saturates, Aromatics, Resins, and Asphaltenes;
SDA	Solvent De-Asphalting
SpGr	Specific Gravity
SQE	Sum of Squared Error
SSE	Sum Squared Error
t	Ton
TAN	Total Acid Number
TBP	True Boiling Point;
TC	Thermal Cracking
UL	Upper Level condition
VB	Vis-Breaking
VGO	Vacuum Gas Oil
VR	Vacuum Residue
WABT	Weight Average Bed Temperature
WHSV	Weight Hourly Space Velocity

C_f	The heat capacity of feed (kJ/kg.°C);
C_h	The heat capacity of hydrogen (kJ/kg.°C);
E_E	the fuel consumption of the re-boiler (m^3/h);
E_f	The fuel consumption for furnace; (m^3/h)
Eff	The thermal efficiency of the furnace (0.685),
E_P	The electrical consumption of the pump (kW);
E_T	The fuel consumption of the turbine (m^3/h);
f^0	flow rate, m^3/h
H_2	Hydrogen
H_2S	Hydrogen disulphide
H_f	The heating value of the local fuel gas equal to 5.327x104 kJ/kg.
k_E	The fuel coefficient (m3/h)
k_P	The energy coefficient (kJ/m3)
k_T	The fuel coefficient (m3/h)
LHSV	Liquid Hourly Space Velocity, h^{-1}
P	Pressure, MPa
QE	The fluid flow rate of the naphtha, kerosene or diesel …, (m^3/h)
QP	The fluid flow rate of the corresponding product; (m^3/h)
T	Temperature, °C
vol	Volume
wppm	weight parts per million
wt.%	weight percent
ρ	Density, kg/m^3

LIST OF APPENDICES

CHAPTER 1: INTRODUCTION

1.1 Background

Heavy crude oils specifications are, high viscosity plus significant amounts of asphaltenes, sulphur, nitrogen and metals (Di Carlo, et al., 1993). Therefore heavy oil has three major problems,

a) Low mobility,

b) High acidity, intensify rectify

c) High content of sulphur and metals.

The needs for processing heavy feedstock into high value products is intensified by the increasing demand on the very limited light oil resources and as a result the light crude oil reserves are decreasing at an accelerating rate.

The steady growing demand fuel can only be rectified by the inclusion of heavier feedstock into refinery operations(Hsu & Robinson, 2006), this feedstock can then be converted into a lighters one by using thermal and/or catalytic processing in the absence or presence of hydrogen pressure. Some of these processes are shown in Table 1.1 & Figure 1.1 (Castaneda et al., 2012)

Table 1.1: Upgrading processes and basic definitions (Gary et al., 2007; Gray, 2007; Rana et al., 2007)

Upgrading	Technology	Catalysts	Definition	Products
Thermal Cracking	Vis-breaking	Non-catalysts	Process: soaking	Liquid products: contain sulfur, nitrogen and metals
	Delayed coking		Decomposed in an oxygen-free environment.	Gas vapor and solid coke.
	Fluid coking and flexi-coking		coke carries heat from burner to reactor	gases, distillates and coke
	Fluid catalytic cracking (FCC)	Catalyst	Catalysis thermal conversion	high gasoline
	Hydro-conversion/ Hydro-pyrolysis		High pressure hydrogen plus the process of catalytic cracking	Higher lighter products because of presence of hydrogen
Hydrogen addition	Hydrocracking	Catalyst	Gas oils or de-asphalted feeds. High pressure catalytic process; cracking + hydrogenation simultaneously	gasoline production
	Hydro-treating		gas oils, kerosene and naphtha produced from bitumen	HDS>90%, HDM,HDN >70%
Advance	Solvent de-asphalting and supercritical extraction	Non-catalyst	addition of a solvent such as propane, butane, pentane or hexane	De-asphalted oil
	Gasification		Steam at high temperatures (>1000^{o}C).	syngas, carbon black and ash
	Novel hydro-visbreaking and fast pyrolysis		viscosity reduction	On-going research

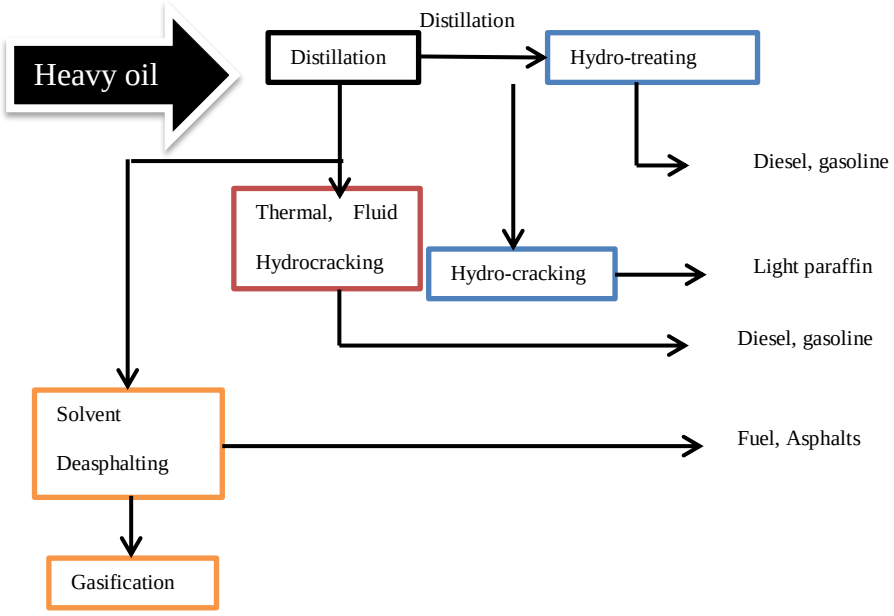

Figure 1.1: Typical pattern for heavy oil (and bitumen) upgrading (Parkash, 2003)

Hydro-treating the process that uses hydrogen and catalyst to remove sulphur from heavy oil has become one of the most attractive technologies for upgrading heavy oil in the world. In hydro-treating research, temperature, pressure and LHSV are three main factors which are critical in the decision making process. Increasing the temperature and pressure while decreasing the LHSV improves the quality of the upgrading process and certainly this will simultaneously increase the operation's expenditure(Gary et al., 2007).

Iran, with 150 billion barrels of overall daily oil production is the third largest oil producer in the world.

Iranian oil production comprises of both conventional and unconventional energy sources. Among the unconventional sources, the heavy oil reservoirs represent the key asset to secure the future of the Iranian energy supply (most of the Iranian proven oil reserves are unconventional oil deposits).

This study presents an optimized model by which, based on the technical, cost efficiency and constraints can identify and propose the most suitable strategy for the upgrading process and meet the market demands in Iran.

1.2 Problem Statement

Iran is endowed with large resources of light oil reservoirs with the APIs' ranging from 30 to 35 and heavy oil with an API of 31. However there are reservoirs with heavier oil such as SOROOSH with an API of 19.3 (Table 1.2). This reservoir produces 50,000 BPSD.

Since refineries in Iran are specifically designed for light oil processing, feeding heavy oil such as oil from the SOROOSH reservoir will spawn challenges and unexpected intricacies.

Therefore some treatment is required before letting the heavy oil enter to the refineries, but this treatment should be carried out under optimum conditions in order to be economically desirable. (Akhavan et al., 2011)

Table 1.2: Typical Properties of Iranian Heavy oil (Akhavan et al., 2013)

Crude		Iranian heavy oil	SOROOSH heavy oil
API		31.6	19.3
Sulphur	%wt.	1.6	3.9
Viscosity	cSt@50^{o} C	8.1	96
Metal	wppm	100	143
TAN	Mg KOH/g	0.07	1.10
Atmospheric Residue (370^{o} C)	%wt. of crude	49.2	65.4
Vacuum Residue (550^{o} C)	%wt. of crude	24.7	40.3

1.3 Objectives and Scopes

The purpose of this study is to develop a techno-economic model for upgrading heavy oil which integrates (i) a specially developed innovative hydro-treatment system

(represented by a three main parameters model) with (ii) an economical evaluation system.

The techno-economic model enables the study of the project to be carried out economically with the assumption of 50,000 BPSD SOROOSH heavy oil being upgraded.

In addition, the impact of the impurities of heavy oil composition and volume on upgrading process conditions will be assessed by an experimental study.

An upgrading heavy oil process model will then be developed to determine the plant efficiency and production specification. Finally, an economic study will determine the corresponding production costs. This model can be used as a decision-making tool for investors and/or project developers who could use it to identify the upgrading plant operating conditions that economically seem sensible.

This study also investigated whether upgrading of heavy oil could open new markets and increase revenues for Iran.

To achieve this, we implemented a pilot plant in RIPI, based on, what is believed to be, the best upgrading technology (Hydro-treatment). This pilot plant was used for testing and improving the upgrading Iranian heavy oil. The pilot plant served as a tool for various objectives as stated below:

To identify the influence of operating conditions on the upgrading process to optimize the parameters for high quality synthetic crude oil production.

The research seeks the answers for the following questions:

1. Does the SOROOSH feedstock, by undergoing the hydro-treatment operating conditions, meet the desired specifications for the Iranian refineries?
2. What is the best process condition that leads to optimum conversion efficiency?
3. What is the related production cost?

1.4 Organization of Thesis

This thesis is divided into 6 Chapters. Following this introductory chapter, literature review is presented in Chapter 2. Then in Chapter 3, the research methodology, and source of data and objective function models are presented.

In Chapter 4, required data to develop a pilot model is presented, and after a discussion on the results obtained from the pilot scale experiments, the effects of the variables on the process are explicated. By solving the functions, the upper and lower levels of optimum conditions are determined.

Chapter 5 is consigned to present an economical model to evaluate the final price for upgraded SOROOSH oil and compare it with some price references. An economical analysis of the process is also presented.

At the end, the conclusions and recommendations for the possible future works are presented in Chapter 6.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Nowadays, with the depletion of conventional light crude oils and more availability of the unconventional ones and growth of oil demand in 2013 in average of 90.6 million compared with 89.9 million b/d last year, made researchers focusing more attention on developing suitable technologies for upgrading heavy oil and improving the crude oil quality, meanwhile environmental issues.(Conglin & Laura, 2013) ;(Nares et al., 2007)

This chapter presents a comprehensive literature review of several upgrading heavy oil processes technologies based on carbon rejection and hydrogen addition (old and recently), conditions and licensors are described.

The major upgrading technologies can be divided in two general routes (a) carbon rejection and (b) hydrogen addition according to some authors. (Joshi et al., 2008).

The first category is a thermal type of processing in which carbon is massively produced, separated from the liquid hydrocarbons, with no incorporation of hydrogen. Carbon rejection processes embrace: thermal cracking, such as coking, and residue fluid catalytic cracking (Gray, 1994);(Speight, 2004). The second route, generally known as hydro-processing, is a type of process in which a catalyst is employed in the presence of elevated hydrogen pressures in order to: a) promote the incorporation of hydrogen into the hydrocarbon matrix; b) remove heteroatoms (sulphur, nitrogen, oxygen, etc.); c) reduce the amount of coke formed during the upgrading process; and accordingly, d) increase the marketing value of the crude oil. (Billon & Bigeard, 2001); (Dufresne et al., 1987; Speight, 2004)

For heavy oils and bitumen, the main drawback of carbon rejection processing is the high amount of low value material, coke that is generated because heavy oils and bitumen usually contain about 50 %wt. of residue fraction, a fraction that boils at

temperatures higher than 545 ºC (Altgelt, 1994). More recently the increased production of heavy oils has turned carbon rejection processes (typically the refiner's first choice for conventional oils) as unsustainable technologies mainly due to more stringent environmental regulations. Consequently, hydro-processing is becoming the best option to avoid coke formation in the upgrading of heavy fractions (Ancheyta & Speight, 2007)

Other way to classify these technologies is by the presence or absence of a catalyst (Kovac et al., 2006; Rana et al., 2007).

Both classifications are quite similar; figure 2.1 present a summary of those. All these processes have good features for specific applications. The catalytic process allows higher conversion than the thermal ones with the following order: Hydro-processing >Residuum Fluid Catalytic Cracking (RFCC) > Fluid Coking (FC) > Delayed coking (DC)>Vis-breaking (VB).

When upgrading unconventional feed-stocks, hydro-conversion is one of the best options to manage the bottom-of-the-barrel residual products.(Runyan, 2007)

However, the selection of one option over the other depends mainly of two factors, a) the refinery configuration and b) the process economy. The process economy is strongly affected by the amount of low value by-products and the amount of hydrogen required. The following sections present some details concerning this type of processes.

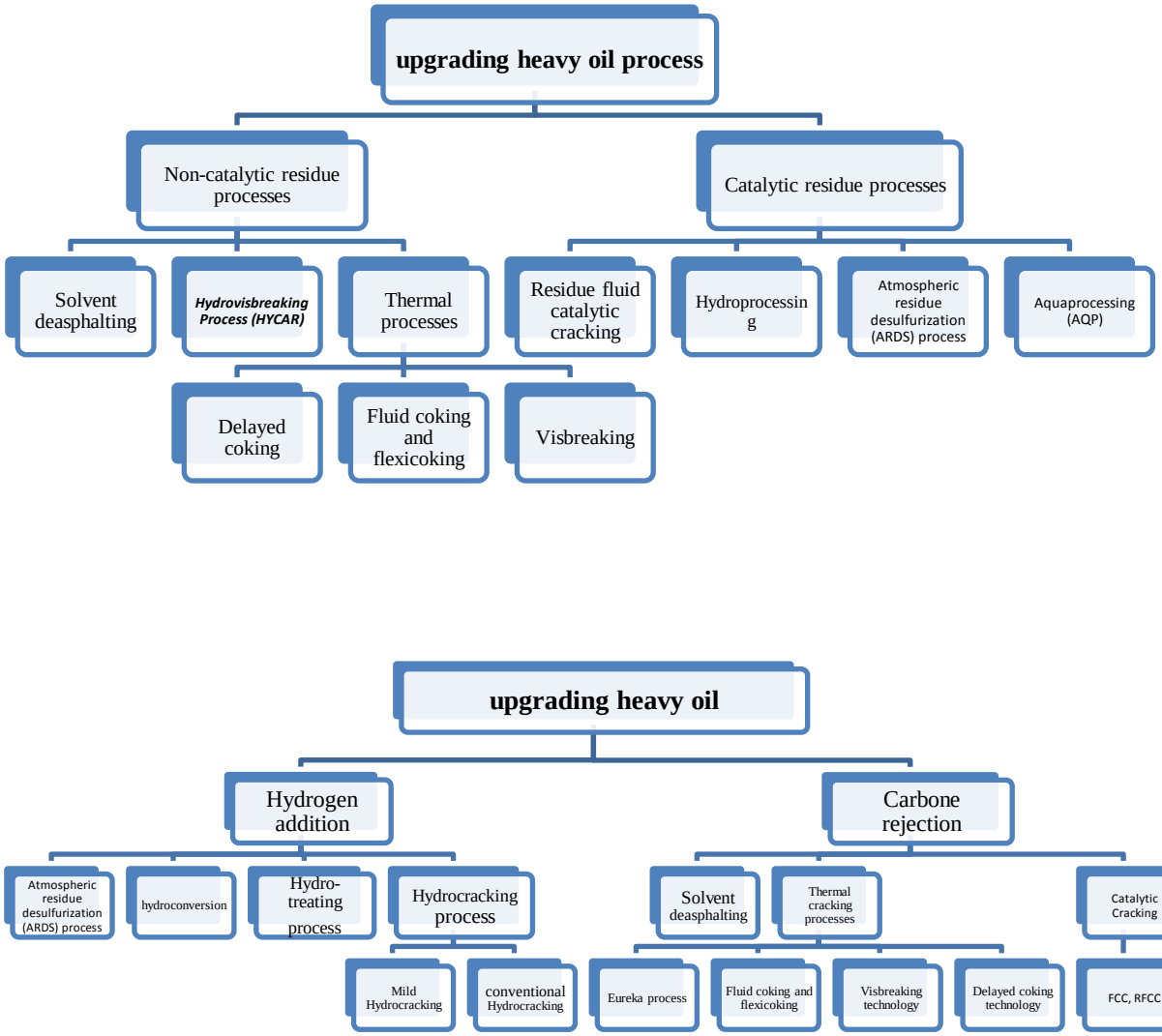

Figure 2.1: Classification of residue upgrading processes (Rana et al., 2007)

2.2 Thermal Cracking Process

Thermal cracking (TC) (non-catalytic) processes offer attractive methods of conversion of heavy feed-stocks because they enable low operating pressure, while involving high operating temperature, without requiring expensive catalysts. Also in general, thermal cracking route is more commonly employed in processing vacuum residues, as compared to hydrogen addition route, because vacuum residues typically

have high content of heteroatoms, metals and asphaltene that pose problems for hydrogen addition processes. But we can find two major disadvantages in these processes; first the conversion in thermal carking is low and limited by the large yield of coke and by products with a low value in the market and the second is the stability of the liquid products which may require further processing. (Speight, 2007; Speight., 2013)

The major variables that affect TC processes performance are: feedstock type, reaction time, temperature, and pressure.

Currently, the most widely operated heavy feedstock conversion processes are vis-breaking and delayed coking, and these processes are still attractive processes for refineries from an economic point of view.

The majority of the thermal cracking processes use temperatures of 455^{o}C to 540^{o}C (850F to 1005F) and pressure of 100 to 1000 psi. The feedstock (reduced crude) is preheated by direct exchange with the cracking products in the fractionating columns. Cracking gasoline and heating oil are removed from the upper section of the column. Light and heavy distillate fractions are removed from the lower section and are pumped so separate heaters. Higher temperatures are used to crack the more refractory light distillate fraction. The streams from the heaters are combined and sent to a soaking chamber where additional time is provided to complete the cracking reactions. The cracked products are then separated in a low-pressure flash chamber, where a heavy fuel oil is removed as bottom.

Mild cracking conditions, with a low conversion per cycle, favour a high yield of gasoline components, with low gas and coke production, but the gasoline quality is not high, whereas more severe conditions give increased gas and coke production and reduced gasoline yield (but of higher quality). With limited conversion per cycle, the heavier residue must be recycled, but these recycled oils become increasingly refractory

upon repeated cracking and if they are not required as a fuel oil stock they may be coked to increase gasoline yield or refined by means of hydrogen process.

The thermal cracking of higher-boiling petroleum fractions to produce gasoline is now virtually obsolete. The antiknock requirements of modern automobile engines together with different nature of crude oils (compared with those of 50 or more years ago) have reduced the ability of thermal cracking process to produce gasoline on an economic basis. Very few new units have been installed since the 1960s and some refineries may still operate the older cracking units.

2.2.1 Delayed Coking Technology

Delayed Coking (DC) is the preferred thermal cracking process to upgrade the bottom of the barrel (from atmospheric and vacuum distillation of crude oil) into liquid and gas product streams leaving behind a solid concentrated carbon material, petroleum coke, because of the process inherent flexibility to handle any type of residua. The term “delayed” comes from the extended period of time given to the cracking reactions to proceed to completion in coke drums(Sawarkar et al., 2007; Wiehe, 2008).

Two major reactions are involved during the DC process: thermal cracking and polymerization. The thermal cracking reaction is responsible for breaking or decomposing the high molecular weight molecules into smaller and lighter ones. The reaction is highly endothermic and the coker heaters supply the heat necessary to initiate the cracking reaction. On the other hand, the polymerization reaction will combine the small hydrocarbon molecules to form a single large molecule of high molecular weight. The ultimate result of this reaction is the formation of coke. Polymerization reactions require long reaction time and the coke drums provide the necessary residence time for these reactions to proceed to completion (Sawarkar et al., 2007; Wiehe, 2008). Nowadays several contributions have been made to improve this technology most of

them led by Foster Wheeler and Conoco-Phillips. The more typical problems during the operation of DC units are: a) foaming in the drum, b) shot coke, c) coking of the heater tubes and d) coking-fouling of the fractionators (Sawarkar et al., 2007; Wiehe, 2008)

2.2.2 Fluid Coking/Flexi-Coking

Fluid coking /Flexi-coking are fluid bed processes developed from fluid catalytic cracking (FCC) technology. Fluid as well as Flexi-coking technologies are comparatively front runner technologies in residue processing. In these processes, circulating coke carries heat from the burner back to the reactor, where the coke serves as reaction sites for the cracking of the residua into lighter products. Fluid coking can have liquid yield credits over delayed coking. The shorter residence time can yield higher quantities of liquids and less coke, but the products have lower quality. Flexi-coking is an extended form of fluid coking and uses a coke Gasifier to convert excess coke to syngas, but the temperature (1000^{o}C) used is insufficient to burn all the coke. Fluid coking is a vaguely better process than delayed coking because of the advantage of a slightly improved liquid yield, also because delayed coking has higher utilities cost and fuel consumption.(Rana et al., 2007)

2.2.3 Eureka Process

The Eureka process is a commercially proven thermal cracking process that produces valuable cracked oil and aromatic petroleum pitch from vacuum residues. Unlike conventional coking processes, Eureka is designed to prevent oil from over-cracking by continuously stripping the products. This results in a relatively high liquid yield and a low gas yield. The residual product from the process is in the form of pitch, which flows easily out of the reactor at the reaction temperature. (Al Humaidan et al., 2013)

2.2.4 Vis-breaking Technology

Vis-breaking (VB) is a mature low-conversion-thermal process could be used to reduce the viscosity of residue to allow the products to meet fuel oil specifications and able to upgrade different feedstock such as atmospheric residue, vacuum residue and even solvent de-asphalted oil, by improving the viscosity of the products. The process name of "Vis-breaker" refers to the fact that the process reduces (i.e., breaks) the viscosity of the residual oil. Therefore, it increases the proportion of middle distillates in the refinery output. (Joshi et al., 2008; Wiehe, 2008)

The major difference between both VB and DC technologies is that VB is a continuous flow process that cannot tolerate significant coke formation, and it requires operating within the coke induction period, which may limit conversion. (Kataria et al., 2004; Speight, 1998; Wiehe, 2008)

It has been reported, that the feedstock composition (properties like paraffin and asphaltenes content as well as aromaticity and hydrogen to carbon ratio) plays an important role to define the operational parameters for a Vis-breaking operation. The asphaltenes content is a critical point that may be directly responsible for the coke formation accordingly with the results reported by Yan (1990). Other authors reported that feeds with initial high resins and asphaltenes content have higher tendencies to form coke than paraffinic feeds when both are subjected to the same operating conditions of treatment.(Tables 2.1 and 2.2)

Table 2.1: Examples of product yields and properties from Vis-breaking Athabasca tar sand bitumen and feedstock having a similar API gravity (Speight & Ozum, 2002)

	Arabian Light Vacuum Residuum	Arabian Light Vacuum Residuum	Iranian light vacuum residue	Athabasca Bitumen
Feedstock				
API gravity	7.1	6.9	8.2	8.6
Carbon residue(a)	20.3		22.0	13.5
Sulphur, %wt.	4.0	4.0	3.5	4.8
Product yields (b) vol%				
Naphtha (<425 F, <220C)	6.0	8.1	4.8	7.0
Light gas oil(425F to 645F, 220C to 340 C)	16.0	10.5	13.1	21.0
Heavy gas oil(645F to 1000F, 340C to 540 C)		20.8	(b)	35.0
Residuum	76.0	60.5	79.9	34.0
API gravity	3.5	0.8	5.5	
Carbon residua(a)				
Sulphur, %wt.	4.7	4.6	3.8	
(a)Conradson				
(b) A blank product yield line indicates that the yield of the lower boiling product has been included in the yield of the higher boiling product				

Table 2.2: Comparison of Vis-breaking with Delayed Coking and Fluid Coking (Speight & Ozum, 2002)

Vis-breaking	
purpose	To reduce viscosity of fuel oil to acceptable levels
	Mild(470C to 495 C; 880 F to 920 F) heating at pressure of 50 to 200 psi
	Reactions quenched before going to completion
	Low conversion(10%) to products boiling less than 220C(430 F)
	Heated coil or drum(soaker)
Delayed Coking	
Purpose	To produce maximum yields of distillate products
	Moderate (480 C to 515 C; 900 F to 960 F) heating at pressures of 90 psi
	Reactions allowed to proceed to completion
	Complete conversion of the feedstock
	Soak drums(845 F to 900 F) used in pairs (one on stream and one off stream being de-coked)
	Coked until drum solid
	Coke removed hydraulically from off-stream drum
	Coke yield: 20%-40% by weight(dependent upon feedstock)
	Yield of distillate boiling below 220C(430F): Ca 30% (but feedstock dependent)
Fluid Coking	
purpose	To produce maximum yields of distillate products
	Severe(480C to 565C ; 900 F to 1050 F) heating at pressures of 10 psi
	Reactions allowed to proceed to completion
	Complete conversion of the feedstock
	Oil contacts refractory coke
	Bed fluidized with stream; heat dissipated throughout the fluid bed
	Higher yields of light ends(<C5) than delayed coking
	Less coke make than delayed coking(for one particular feedstock)

The main operating conditions for thermal processes are compiled in Table 2.3. Liquid products obtained from thermal processes contain sulphur, nitrogen and metals (V, Ni, etc.) that indeed need further purification by hydro-treatment (HDT) process like hydro-desulfurization (HDS), Hydro-denitrogenation(HDN) and Hydro-demetallization (HDM) respectively.(Biasca et al., 2003; Speight, 2004)

Table 2.3: operating conditions for thermal processes (Biasca et al., 2003; Speight, 2004)

Residue technology	Licenser	Operating conditions	
		Temperature (^{o}C)	Pressure (MPa)
Delayed coking	ABB LUMMUS	480–515	0.61
	FOSTER Wheeler/ UOP		
	ConocoPhillips		
Vis-breaking	ABB Lummus	450–510	0.34–2.0
	Global		
Fluid coking	ExxonMobil	480–565	0.07
Flexi-coking	Conoco-phillips	830–1000	
	Halliburton KBR		
Gasification	Chevron Texaco	>1000	

2.3 Solvent De-asphalting

The residue contains high concentration of asphaltene, which can be solvent de-asphalted by a separation process. Solvent De-asphalting (SDA) is a unique separation process in which residue is separated by molecular weight (density) instead of by boiling point. SDA process produces low contaminant De-asphalted oil (DAO) that is rich in paraffin type of molecules. SDA has the advantage of being a relatively low cost process that has flexibility to meet a wide range of DAO qualities. During SDA process, the feed is mixed with a light paraffinic solvent (propane, butane, pentane, or n-heptane), where the oil is solubilized in the solvent. The insoluble pitch will precipitate out of the mixed feedstock as asphaltene. The separation of the DAO phase and the pitch phase occurs in the extractor. The extractor is designed to efficiently separate the two phases and minimize contaminant entrainment in the DAO phase. At a constant solvent composition and pressure, a lower extractor temperature increases the DAO yield and decreases the quality. While an increase in solvent the DAO yield remains constant and improves the degree of separation of individual components and results in the recovery of a better quality DAO. The solvent recovered under low-pressure from the pitch and DAO strippers is condensed and combined with the solvent recovered

under high pressure from the DAO separator, which is then recycled back to initial stage. DAO is normally used as FCC and hydrocracking feed-stocks due to its low metal (Ni+V) contents.(Castaneda et al., 2012)

2.4 Residue Fluid Catalytic Cracking (RFCC)

Fluid Catalytic Cracking (FCC) is a well-established approach for converting a significant portion of the heavier fractions of the crude barrel into a high-octane gasoline blending component. RFCC is an extension of conventional FCC technology that was developed during the early 1980, which offers better selectivity to high gasoline and lower gas yield than hydro-processing and thermal processes. Because RFCC requires better feed quality, which makes this process less likely than hydro-processing. In order to control heat balance and to recover part of the heat for steam production, RFCC process design includes two-stage regeneration, mix temperature control and catalyst cooler. The catalyst properties also play an important role to resist metal content and carbon deposition. In this respect catalyst pore structure limits the diffusion of residue on the catalytic sites. The catalyst used for RFCC is of acidic matrix such as crystalline alumina-silicate zeolite (USY or rare earth exchanged HY) in an inorganic matrix, which fulfills the required physic-chemical properties. The major limitation of RFCC process is the need of good quality feed-stocks (high H/C ratio and low metal content), which avoid perverse high coke yield, high catalyst consumption and unit operability. Therefore, this process can only treat atmospheric residue, which predominantly contains relatively low amounts of metals, sulphur and carbon. However, such kind of feeds are limited in refineries, moreover, the crude from which they are derived are high in price.(Rana et al., 2007). Table 2.4 shows the comparison between thermal cracking and catalytic cracking.

Table 2.4: Comparison of Thermal cracking and Catalytic cracking (Speight, 2007)

Thermal Cracking	Catalytic Cracking
No catalyst	Use catalyst
Higher temperature	Lower temperature
Higher pressure	Lower pressure
Free radical reaction mechanisms	More flexible in terms of product slate
Moderate thermal efficiency	Ionic reaction mechanisms
No generation of catalyst needed	High thermal efficiency
Moderate yields of gasoline and other distillate	Good integration of cracking and regeneration
Gas yield feedstock dependent	High yields of gasoline and other distillates
Low-to-moderate product selectivity	Low gas yields
Alkanes produced but feedstock dependent yields	High product selectivity
Low octane number gasoline	Low *n*-alkane yields
Some chain –branching in alkanes	High octane number
Low to moderate yield of C_4 olefins	Chain-branching and high yield of C_4 olefins
Low to moderate yield of aromatics	High yield of aromatics

2.5 Hydro-processing of Residue

Hydro-processing consumes a substantial amount of hydrogen and is relatively high in investment and operating costs compared with thermal processes with the expense of high product selectivity of light products. In addition, hydro-processing offers better selectivity of liquid yield (85% and higher) than any other process discussed above.

Hydro-processing involves many different reactions depending on both reaction conditions and catalysts; thus it includes hydro-treating (HDT), hydro-conversion (HDC) and hydrocracking (HCK); the process can convert heavy oils into high-value products with simultaneous hydro-desulfurization (HDS), hydro-denitrogenation (HDN), hydro-demetallization (HDM) and Conradson Carbon Removal (HDCCR) and asphaltene conversion in the presence of catalysts and hydrogen under high pressure condition. Nowadays, the hydro-processing technology is well established and has been extensively practiced in refineries worldwide.

Most of the hydro-conversion processes require catalyst, except few of them such as hydro-visbreaking. Hydro-processing technologies, including some relevant

characteristics such as: feed type, products, and operating conditions, are summarized in Table 2.5(Billon & Bigeard, 2001; Heinrich & Kasztelan, 2001; Thompson, 2008; Vasquez, 2007). As a general characteristic; the heavier the feedstock the higher must be the severity of the conditions for treatment.

Table 2.5: Summary of hydro-processing characteristics Process (Billon & Bigeard, 2001; Heinrich & Kasztelan, 2001; Thompson, 2008; Vasquez, 2007)

	Feed	Products	Operating Conditions	Remarks
HYD/HDT	All cuts	Same as feed	0.5 – 16 MPa 260 - 400°C 0.15 – 10 h^{-1}	Hydrogenates the feed with 10% or less hydrocracking. Removes sulphur, nitrogen and metals.
HCK	Medium and Heavy cuts	Light gases, Naphtha, Kerosene, Diesel fuel, Lube oils, FCC feed	10 - 20 MPa 350 - 430°C 0.2 – 2 h^{-1}	Changes the skeletal structure of the feed, by breaking C-C bonds
Mild-HCK	Medium and Heavy cuts	Kerosene, Diesel oils, FCC oils	5 - 8 MPa 350 - 440°C 0.2 – 2 h^{-1}	Similar to HCK, but at a lower severity. Hydrocracks 40% or less of the feed

2.5.1 Hydro-treating Process

Hydro-treating (HDT) is a catalytic process in which hydrogen is used to remove heteroatoms as sulphur (HDS) and nitrogen (HDN) and hydrogenation (HYD) from hydrocarbon intermediate streams during the refining processing (e.g., naphtha, middle distillates, reformer feeds, residual fuel oil, and heavy gas oil fractions). Additionally, feeds containing oxygen or metal components are treated to remove such impurities by hydro-deoxygenation (HDO) and HDM, respectively(Heinrich & Kasztelan, 2001). As shown in table 2.6, hydro-treating process is more than half of the other process in world's refiners operations. (True et al., 2013)

Table 2.6: Upgrading Processes in World's Refiners (True et al., 2013)

Region	no of refineries	catalytic cracking	catalytic reforming	catalytic hydrocracking	catalytic hydrotreating
Africa	45	210,380	458,426	61754	833626
Asia	165	3,172,968	2,258,821	1,245,050	10,228,614
Eastern Europe	89	857,911	1,467,171	394,058	4,243,208
Middle East	44	357,550	660,397	596,891	2,047,063
North America	148	6,529,756	4,138,344	1,948,708	16,581,981
South America	66	1,311,007	401,938	132,400	1,904,177
Western Europe	98	2,162,965	2,107,737	1,187,612	10,015,479
Total	655	14,602,537	11,492,834	5,566,473	45,854,148

More than 30 HDT technologies are available for licensing, and most of them have similar process flow configuration (Gary & Handwerk, 2001). In general, these processes can be divided in two main sections: reaction section and separation section.

The reaction section comprises the feeding pump, the hydrogen make up, and the pre-heaters. The feedstock and hydrogen are put together prior to the pre-heaters to guarantee good mixing. Afterwards, the commingled stream passes through the pre-heaters and the furnace where its temperature is increased to the desired reaction temperature. Feedstock and hydrogen are fed at the top of the reactor and distributed through the catalyst bed where the desired reactions take place.

The effluents of the reactor heat the feedstock and are sent to the hot separator where the light hydrocarbons and gases are striped from the heavy products. The gas stream is washed and passed through an amine absorber to remove H_2S from the recycled hydrogen. The mixture of light and heavy hydrocarbons is sent to the distillation section where steam is used to remove the light ends and stabilize the product.

Main operating variables for hydro-treating processes are: the hydrogen partial pressure, reaction temperature, space velocity, the hydrogen recycle ratio and its purity (Heinrich & Kasztelan, 2001).

Hydrogen partial pressure: it plays an important role in the selectivity and performance of the process. Its increase favours the removal of contaminants and avoids deactivation of the catalyst due to coke formation and deposition; however, if it is too high the rates of the desired reaction cannot be considerably improved because of the saturation of the catalyst surface with adsorbed hydrogen, and the investment per unit can be sensitively affected (more resistant equipment); therefore, operating under the most optimum partial pressure of hydrogen, which is related to the type of feedstock that is processed and the desired selectivity, is required.

- Reaction temperature: to achieve constant selectivity and conversion at fixed operating pressure, the temperature in the reactor is increased to compensate the deactivation of the catalyst; thus, a “start of run” temperature and an “end of run” temperature are defined.
- Space velocity: the space velocity represents the quantity of feedstock (in mass or volume) that is processed per unit of catalyst (mass or volume) as: Liquid Hourly Space Velocity (volume) or Weight Hourly Space Velocity (mass).
- Recycle of Hydrogen: the high partial pressure of hydrogen creates an excess of hydrogen in the system that should be recovered and re-injected to the system. Also, it is used as quench to reduce the temperature raise due to the release of heat of the exothermic reactions. The hydrogen recycle ratio varies as a function of the properties of the processed feedstock. In general, higher recycle ratios are used for heavier feedstock.

2.5.2 Hydrocracking Process

Hydrocracking (HCK) is a very useful petroleum refining process that uses hydrogen and catalysts with relatively low temperature and high pressures for converting a wide range of feed-stocks like ; a) naphtha, b) kerosene, c) gas oil, d) vacuum distillate, and

e) deasphalted vacuum residue (Billon & Bigeard, 2001). HCK processing involves simultaneous cracking and hydrogenation of hydrocarbons to produce synthetic fuels with smaller molecules and higher H/C ratios (Gates. et al., 1979).

HCK processing involves simultaneous cracking and hydrogenation of hydrocarbons to produce synthetic fuels with smaller molecules and higher H/C ratios(Gates. et al., 1979). Generally, the process conditions for high conversion HCK (70 – 100 %wt.) are: temperatures of 350-430 C, 8.5-20.0 MPa of hydrogen pressure, 0.5-2.5h^{-1} liquid hourly space velocity, hydrogen-to-oil ratios of 505-1685 nm3/m3, and hydrogen consumption in the range of 200-590 nm^3/m^3 (Scherzer & Gruia, 1996).

Two different HCK processes can be identified: the mild hydrocracking (MHCK) and the conventional (HCK), in each one of them different operating conditions and catalysts formulation can be used, as shown in Table 2.7. The reactions involved in both hydrocracking process are similar, but they have different product distribution. The lower amount of distillates obtained for MHCK are related with the lower hydrogen pressure used for this process compared with the conventional one (Billon & Bigeard, 2001).

Table 2.7: Comparison between the operating conditions for conventional and mild hydrocracking process (Billon & Bigeard, 2001)

Typical Operating Condition	Conventional Hydrocracking	Mild Hydrocracking
Pressure (MPa)	10 – 20	5 – 8
Temperature (ºC)	380 – 430	380 – 440
H2/feed (Nm3/m3)	800 – 2000	400 – 800
Space velocity (h-1)	0.2 – 2	0.2 – 2
Reactor type	Fixed / moving	Fixed /moving
H2 consumption(%wt. of feed)	1.4-4	0.5-1

Hydrocracking is far less common than hydro-treating, but the number of mild hydrocrackers is increasing as refiners build new units to meet clean fuel regulations.

2.5.2.1 Hydrocracking reactions

A complex network of reactions is accountable for the transformation of a feed into lighter products during the HCK process. However, even with the hundreds of simultaneous reactions occurring during HCK of petroleum; most of the authors described the mechanism as catalytic cracking with hydrogenation super imposed (Billon & Bigeard, 2001; Gary, 2003; Gary et al., 2007). Both reactions are complementary; the cracking is endothermic or slightly exothermic while the HYD is exothermic. The global HCK reaction is exothermic; the amount of heat produced is higher than the amount consumed (Gary et al., 2007). According to Billon & Bigeard (2001) the HCK reaction can be divided into two groups. In the first group, most of the reactions accountable for the hydro-treating process can be included, such as: HDS, HDN, and aromatics HYD. For instance, the sulphur removal is almost completed under HCK conditions compared to the nitrogen removal; the aromatic hydrogenation reaction is the initial step for cracking cyclic hydrocarbons. The hydrocracking reactions (splitting C-C bonds) and the hydro-isomerization reactions (C-C rearrangement reactions) are grouped in the second set of reactions. The C-C bonds can be broken in

different ways depending of their position. Billon and Bigeard (2001) suggested the following types of reaction during hydrocracking: a) simple hydrocracking reactions, a C-C bond in a chain is cracked, b) hydro-dealkylation, a C-C bond adjacent to a ring is cracked and c) ring opening reaction, in which a C-C bond in a ring is cracked. As previously mentioned, the aromatics HYD is a critical reaction to crack cyclic hydrocarbons, the cracking of aromatic compounds goes first via a HYD step followed by the cracking of the ring. Actually, under the typical operating conditions used for HCK it is impossible to crack an aromatic ring, but the naphthenic produced can be converted at these conditions(Billon & Bigeard, 2001). The aromatic hydrogenation reactions are very exothermic, so they are not thermodynamically favoured at high temperatures. As the reaction temperature increases more aromatic compounds are in the products, at that point the reaction is controlled by the equilibrium. For the aromatic hydrogenation, under hydrocracking conditions, the overall aromatics-saturation is controlled by the aromatic concentration, hydrogen partial pressure and the temperature.

2.5.2.2 Hydrocracking process

The operating conditions and the catalysts for HCK are selected according to the feedstock to be processed and the end product required. Taking that into consideration, several HCK flow schemes have been proposed. These schemes can be grouped into two types: a) one stage process and b) two stages process. In each one of these HCK schemes two main sections are identified: 1) a high pressure section that comprises heating devices for the feedstock, reactors and gas liquid separators; and 2) a low pressure section to fractionate the products(Billon & Bigeard, 2001; Gary, 2003; Gray, 2002). Commonly, HDT or “guard” reactors remove any impurities that can poison the HCK catalyst.

Typically, HCK reactors are fixed bed with internals and configuration similar to HDT reactors to: distribute the feedstock, support the catalyst, and remove the excess energy. However, the development of alternatives processes for conversion of heavier feed-stocks under more extreme operating conditions required the design of new reactors that allow for compensation of the rapid deactivation of the catalyst; thus, moving or Ebullated bed reactors stands as the main alternative. In Ebullated bed reactors the feedstock enters through the bottom and flows upward keeping the catalyst under suspension. The catalyst is typically less than one millimetre in size to facilitate its suspension. There are two of these processes available for licence today LC-Fining and H-Oil. The main operating variables for HCK processes are hydrogen partial pressure, catalyst bed temperature, hourly space velocity of the feed and hydrogen recycle ratio. They are adjusted to improve conversion, selectivity and product quality; and to increase the catalyst life. Moreover, for HCK processes that work with Ebullated bed reactors an additional important variable is related to the catalyst replacement. Table 2.8 shows some of the HCK processes available for licensing; all of them use fixed-bed reactors with liquid down-flow (trickle-bed reactor). H-Oil and LC-Fining have been already described as Ebullated-bed technology.

Table 2.8: Hydrocracking Processes available for License (Gray, 2002)

Process	Company
Isomax	Chevron and UOP, LLC
Unicracking	UOP
GOFining	Exxon Research and Engineering
Ultracraking	BP Amoco
Shell	Shell Development Co
BASF-IFP hydrocracking	Badische Anilin und Soda Fabrik, and Institute Francais Petrole
Unibon	UOP, LLC

2.5.2.3 Modeling of Hydrocracking process

Hydrocracking is a catalytic chemical process which converts high-boiling hydrocarbons to more valuable lighter products like diesel, kerosene, naphtha and light

ends. Hydrocracking is carried out in multiple catalytic beds in the presence of excess hydrogen at high temperatures and pressures. During hydrocracking, large compounds are broken to form low molecular weight compounds. When the reaction takes place over a catalyst in a hydrogen-rich atmosphere, other reactions, such as HDS, HDM, etc., occur simultaneously. The different rates and selectivity of each reaction depend on the properties of the catalyst used and on the reaction severity. This process involves the use of bi-functional catalysts at temperatures around 370–450 °C with relative high hydrogen pressure of the order of 10-14Mpa(Speight, 2004).

Figure 2.2 illustrates the scope of published HC models classified according to a three-layer onion. The core of the onion is the kinetic model, focusing on the micro kinetic analysis of reaction mechanisms. It allows for the study of the catalyst selection, feedstock effect, and influence of reaction conditions. The reactor model quantifies the reactor performance (e.g., product yield and fuel properties) under different operating conditions, such as flow rate, temperature profile, and hydrogen pressure. It helps the refiner determine the optimal unit operations. A process model aids in the optimization of plant-wide operating conditions to maximize the profit, minimize the cost, and enhance the safety.

Various reviews on hydrocracking technology have been reported in the literature. Probably the first complete review was done by Choudhary & Saraf (1975). Different aspects of hydrocracking were discussed, such as types of hydrocracking, catalysis, effects of feed, catalyst acidity, pore diffusion, and catalyst poisons on hydrocracking reactions. Some of the general points of distinction among the major hydrocracking processes were also discussed. (Ancheyta, Sanchez, et al., 2005). Mohanty et al.,(1990) reviewed the technology, chemistry, catalysts, kinetics, and reactor modeling of hydrocracking.

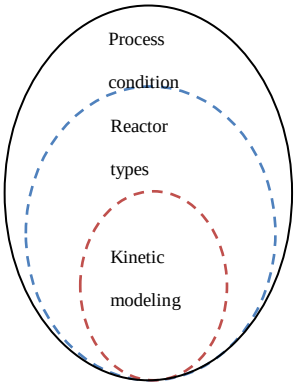

Figure 2.2: Three-layer onion for modeling scope

Neither kinetic models nor reactor modeling were described with enough detail, since the authors only summarized the main characteristics of the reported models. They recognized that considerable information has been published on the hydrocracking of pure hydrocarbons, in contrast with the very few reported studies on kinetics and reactor modeling of petroleum fractions hydrocracking. The development of robust kinetic models of heavy oil hydrocracking is not straightforward due to the complexity of these hydrocarbon feed-stocks, the analysis of its components as well as the complex reaction networks (Rana et al., 2007).

Kinetic modeling is the core of optimal work, which can predict the performance of the hydrocracking process within the operating severity and investigate the performance behavior beyond the experimental domain.

Different approaches have been reported for kinetic modeling of heavy oil hydrocracking, although the most commonly used method is the lumping technique(Sanchez et al., 2005; Fukuyama & Terai, 2007; Martinez & Ancheyta, 2012).

Chaudhuri et al. (1995) discussed the state-of-the-art of mild hydrocracking processes, including data characterization reactivity's, reaction networks, and kinetics. Comparisons were made between hydrocracking and mild hydrocracking. Only a few kinetic models for hydrocracking were mentioned. These authors concluded that the

complexity of the industrial feed-stocks suggests that the use of pseudo-components would continue in the study of reaction kinetics.

Another review of hydrocracking has been reported by Valavarasu et al. (2003), who focused their contribution on important aspects of mild hydrocracking, such as processes, catalysts, reactions, and kinetics.

Predicting the products distribution in conversion processes is essential to maximize the desired product yield. Such prediction is normally achieved by utilizing a reliable kinetic model that can accurately anticipate the product yields at different operating conditions. However, the identification of the exact chemical reactions involved in conversion processes is very difficult. Therefore, a simplified modeling approach, namely the discrete lumping, is normally adopted to overcome the modeling complexity. (Al Humaidan et al., 2013)

In this modeling approach, the heavy feedstock and the complex product are divided into pseudo-components or lumps, in which the chemically similar species are combined and involved in various parallel and series reactions. The selection of pseudo-components can be based on product slates, true boiling point, carbon number, or molecular weight. Although the discrete lumping models have limited accurate predictive power, their predictive performance is quite sufficient for many applications (Schweitzer et al., 1999; Ancheyta & Sotelo-Boyas, 2000; Martens & Marin, 2001; Balasubramanian & Pushpavanam, 2008; Al humaidan et al., 2010) . The success of discrete lumping models is mainly due to their ease of application and incorporation into reactor models of process simulators. The shortcomings of this modelling approach, however, are the rapid increase in the number of kinetic parameters as the number of lumps increases and the time consuming adjustment of rate parameters for each feedstock (Martens & Marin, 2001).

Takatsuka (Takatsuka et al., 1989) initiated the effort by developing a lumping model that has eight lumps, four of these lumps represent the polymerization and condensation of residue and the other four represent the cracked products. They identified the key independent variables in residue thermal cracking as: reaction temperature, reaction pressure, residence time, residence time distribution, and feedstock properties.

A discrete lumping model for the thermal cracking of vacuum residue was also developed by Del Bianco et al. (1993). Their proposed model is mainly composed of three pseudo-components; namely vacuum residue, distillate, and coke. They reported that distillate production can be described by a simple first-order reaction, while coke formation results from a number of consecutive reactions, in particular involving asphaltenes.

Asgarzadeh (Asgharzadeh et al., 2011) also presented a three-lump kinetic model that determines the yields of gas, liquid, and solid during the thermal cracking of vacuum residues. They found that the activation energies for cracked oil production are greater than the activation energies of gas formation, which suggests higher tendency for cracked oil production as the temperature increases.

Martinez (Martínez et al., 1997) developed a three-lump kinetic model (gas, oil and coke) for the decomposition of asphaltenic residue obtained from coal liquefaction, and reported second order kinetics. They attributed the poor prediction of their model at high cracking temperature (475°C) to the significant increase in secondary formation of coke from the produced oil.

Kataria et al., 2004 and Singh et al. (2005) developed five-lump kinetic models that describe the thermal cracking of vacuum residue in visbreaking process. Both models utilized the experimental data reported by Singh et al. (2005) and reported first-order kinetics for the thermal cracking reactions. Singh et al.(2005) refined their earlier five-

lump model to a four-lump model, which has limited applicability (i.e. long residues only)(Singh et al., 2012).

Zhou (Zhou et al., 2007) developed a kinetic model of 11 lumps to predict the yield of delayed coking at different operating conditions. Maciel & Sugaya (2001) also applied the lumping approach to develop computer aided tools that examine the performance of an industrial delayed coking unit. Gary et al., (2004) proposed a lumped kinetic model to describe the kinetic of cracking and devolatilization during the thermal cracking of Athabasca residue. Radmanesh (2008) further improved this model to account for the experimental observation related to coke yield. Jia (2009) developed a thermal cracking kinetic model for in situ upgrading of various heavy crude oil by combustion. The model described the kinetic mechanisms and concentration changes of individual species in the thermal cracking reactions.

The main advantages of the lumping technique are its easy computational implementation and small amount of data required for parameter estimation. The more lumps the better description, but increasing the number of lumps also increases the number of parameters to be estimated. Lumping has been successfully applied for modelling hydrocracking of heavy oils. The main drawback when using lumping technique is the determination of each lump properties such as density, viscosity, molecular weight, distillation curve, among others which are needed to perform mass and energy balances since they are continuously changing inside the reactor. This method has been used extensively for hydro-treating and hydrocracking reactions (Mohanty et al., 1991; Ayasse et al., 1997; Sanchez et al., 2005; Fukuyama & Terai, 2007).

Another kinetic model was proposed to describe the atmospheric residue hydro-conversion with a dispersed catalyst in a batch reactor under the reaction conditions of 420 or 430 °C, an initial partial pressure of hydrogen of 15 MPa, and different reaction

times. The model, taking into account the gas–liquid mass transfer, includes hydrogen and five lumps: remaining residue (>510 °C), VGO (350–510 °C), distillate (180–350 °C), naphtha (40–180 °C), and gas. Vapor–Liquid Equilibrium (VLE) was determined by performing an adiabatic flash with PROII software.(Nguyen et al., 2013)

Five-lump models for kinetic modeling of hydrocracking of vacuum residue, VGO and middle distillates have been reported by many authors, (Callejas & Martinez, 1999; Sanchez et al., 2005; Jarullah et al., 2011; Zhou et al., 2011; Martinez & Ancheyta, 2012) (Figure 2.3)

These models have different reaction rate coefficients, makes a distinction of different hydrocarbon groups based on boiling ranges, and includes the following lumps: unconverted vacuum residue (538^{o}C), vacuum gas oil (VGO; 343–538^{o}C), middle distillates (204–343^{o}C), naphtha (IBP-204^{o}C), and gases. These kinetic studies have been carried out in a CSTBR, trickle bed reactors in different conditions.

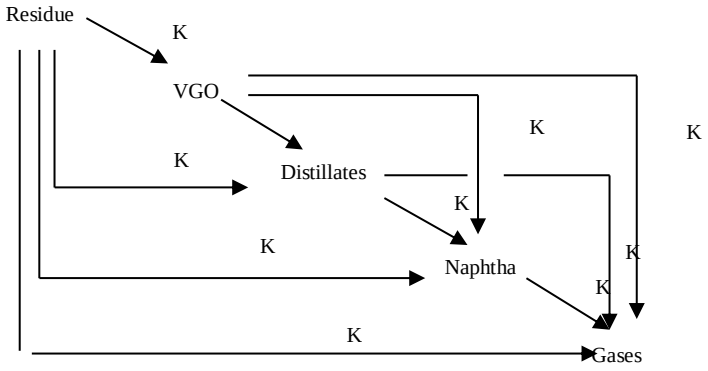

Figure 2.3: Propose Kinetic model for the hydro-conversion of heavy oils

Table 2.9 summarizes the key features of well-known published HCR models based on non-molecular composition lumping.

Table 2.9: Key Features of Published HCR Models Built by Lumping Based on Non-molecular Composition

Model scope	lumping technique	data source	data requirement (feed)	data requirement (product)	reactor operation	product yield	fuel quality estimation	Ref
kinetic model	2 lumps	lab	no	yield	N/A	yes	N/A	(Qader & Hill, 1969)
kinetic model	4 lumps	Lab	no	yield	N/A	yes	N/A	(Valavarasu et al., 2005)
kinetic model	5 lumps	pilot	no	yield	N/A	yes	N/A	(Sanchez et al., 2005)
kinetic model	37 lumps	lab	TBP curve/SARA analysis/ elemental analysis of C, H, S, N, O, Ni, and V	yield/TBP curve/SARA analysis/ elemental analysis of C, H, S, N, O, Ni, V	N/A	yes	N/A	(Verstraete et al., 2007)
kinetic model	discrete lumps	Pilot /commercial	TBP curve	yield/TBP curve		yes	TBP curve	(Stangeland, 1974)
reactor model	discrete lumps	commercial	TBP curve/density	yield/TBP curve	temperature profile/ hydrogen consumption	yes	N/A	(Mohanty et al., 1991)
reactor model	discrete lumps	commercial	distribution	yield/TBP curve	temperature profile/ hydrogen consumption	yes	N/A	(Pacheco & Dassori, 2002)
reactor model	discrete lumps	commercial	TBP curve/density	yield/TBP curve	temperature profile/ hydrogen consumption	yes	N/A	(Bhutani et al., 2006)
kinetic model	continuous lumping	Pilot	TBP curve	yield/TBP curve	N/A	yes	N/A	(Laxminarasimhan et al., 1996)
reactor model	continuous lumping	commercial	TBP curve/PNA distribution along with TBP curve	TBP curve/PNA distribution along with TBP curve	temperature profile/ hydrogen consumption	yes	PNA composition of product	(Basak et al., 2004)
kinetic model	7 lumps	lab	SARA analysis	yield/SARA analysis	N/A	yes	N/A	(Fukuyama & Terai, 2007)

2.5.2.4 Reactor Modeling of Hydrocracking process

Two ideal flow reactors exist that are used for reactor model development (Remesat, 2007)

1. CSTR (continuously stirred tank reactor) = molecules completely mixed and

2. PFR (plug flow reactor) = all molecules leaving reactor have been inside the reactor exactly the same amount of time (flat velocity profile with no axial mixing).

The model of a (non-ideal) reactor needs to portray the real reactor with some realism. The principal characteristics of the reactor that cause its behavior to deviate from the ideal much be reflected accurately in the model. The proper choice of a model to represent a real reactor has been stated as more art than science.

As a first approximation, non-ideal reactors can either be represented as an ideal CSTR or PFR. In real reactors, however, non-ideal flow patterns that represents a loss of conversion and these needs to be accounted for in the reactor model.

A summary of the experimental rigs in batch and semi-batch mode for studying the hydrocracking of heavy oil is presented in Table 2.10

Table 2.10: Experimental setups for hydrocracking of heavy oil (Angeles et al., 2014)

Operation mode	Reactor size (ml)	Liquid loading (g)	Initial H_2 pressure (bar) (Initial pressure without heating)	Operating temperature (◦C)	Reaction time (h)
Batch	30	10	90	410-460	0.5-0.4
Batch	30	10	180-160	380-460	1.5
Batch	300	30	75	430-460	2-10
Batch	30	2	90	410-450	0.25-4
Batch	50	10.4	93	340	0.5-1.5
Batch	N/A	350	70	430	2
Batch	300	50	33	430-460	1
Batch	300	100	103	413	2
Batch	100	30	34.5	320-380	3-48
Batch	100	30	34.5	320-380	3-70
Batch	500	N/A	70	420	1.5
Batch	500	N/A	50	420	1-4
Batch	165	35	N/A	416-436	1-1.25
Batch	N/A	N/A	70	435	1
Batch	100	40	70	430	1
Batch	N/A	143	41.1 & 55	350-400	1-24
Semi-Batch	230	50	80-130 bar and 300 ml/min(*)	430-450	1.5
Batch	50	N/A	69	310-400	1
Batch	30	45	70	340	30-240
Semi-Batch	250	80	138 bar and 900 ml/min(*)	415-445	1
Batch	N/A	N/A	70	420	1
Batch	300	N/A	55	415	1
Semi-batch	250	N/A	138 bar and 900 ml/min(*)	414-445	1
Batch	35	10	60	330	1
Batch	35	10	60	330	1
Batch	136	10	100	410	6-12
Batch	500	150	50-80	420-435	1
Batch	300	80	35	400-430	1
Batch	1000	380	60	420	1
Batch	50	3 &5	61	350	0.5-3
Semi-batch	65	25	138 bar and 4000 ml/min(*)	380-460	0.15-1

(*)=Specification of the flow rate of hydrogen is also required for semi-batch systems

2.5.3 Hydro-conversion Process

In the literature the terms HCK and hydro-conversion (HDC) are sometimes used non-restrictively for the conversion of both vacuum distillates and residues. In the last 50 years some differentiation between the functionally of both process have been reported, the term HDC is used for heavy oil and residue conversion(Sanchez &

Ancheyta, 2007). Typical operating conditions for HDC are far more severe than those for HDT(Morel & Peries, 2001), as presented in Table 2.11. Thus, in addition to the catalytic reactions usually present in HDT processing (HDS, HDN, etc.) one can also observe hydrocracking to light fractions such as: gases, naphtha, and distillates; hydrogen transfer; hydrogenation of polyaromatics; and thermal condensation of polyaromatic radicals.

Table 2.11: Typical operating conditions in residue Hydro-conversion (Morel & Peries, 2001)

Parameter	
Space velocity, h^{-1}	0.1 – 0.5
H_2 pressure, MPa	10 -17
H_2 recycle, std m^3/m^3	600 – 1600
Temperature, ºC	340 - 450

Generally speaking the HDC is defined as the conversion by thermal cracking of carbon-carbon bonds to form free radical molecules (Heck et al., 1992) in the presence of catalysts, hydrogen or a hydrogen donor solvent.

Typical feeds for residue HDC processes are atmospheric and vacuum residues, which have an important content of asphaltenes and metals. These residue components have an impact on the performance of the HDC process, mainly limiting the conversion level (Wiehe, 2008).

The HDC of heavy oils into more valuable streams requires efficient hydrogen activation; which has an important role increasing the coke induction period by terminating free radicals and by reducing the rate of aromatics combination to form larger poly-nuclear aromatics(Ancheyta et al., 2001; Wiehe, 2008). The hydrogen activation dilutes the cracking reactions, without any effect on cracking reactions rate, because the concentration of reactive hydrogen donors is kept only as high as needed, consequently, the products incompatibility presented in thermal cracking processes is avoided; hydro-conversion of vacuum residue can be over 85 wt.%, as opposed to 20 to

30 wt.% for VB and 50 to 60 wt. % for commercial coking(Wiehe, 2008) . According to some authors, the major drawback for HCK and HDC is the cost related with the catalysts and high hydrogen pressure required for the reaction. Some preferences toward thermal cracking process based in these constraints have been expressed. However, an interesting economical comparison made by (Runyan, 2007) for the upgrading of Alberta bitumen using delayed coking and HDC process is reported in Table 2.12. Both processes are compared in terms of product quality, product yields, and net income. The results suggested that HDC is an attractive technology for upgrading these unconventional oils.

Table 2.12: Results for upgraded Alberta bitumen using DC and HDC technologies (Runyan, 2007)

	DC(Gray, 2002)	HDC process
Bitumen feedstock	7.8	8.5
Gravity, API	5.10	5.14
S, wt. %	0.45	0.27
N, wt. %		
Syncrude product	28.7	24.8
Gravity, API	3.20	0.24
S, wt. %	-	0.27
N, wt. %		
Product yields, % Vol		
Light crudes	82.0	90.5
Heavy crudes	0.0	17.5
Coke	18.0	0.0
Light crude process, $/bbl.("Alberta Energy and Utilities Board," 2005)	51.51	51.51
Heavy crude process, $/bbl.	31.57	31.57
Gross revenues, $/bbl.	42.24	52.14
Bitumen prices, $/bbl	30.73	30.73
Operating costs, $/bbl.	4.00	3.5
Hydrogen costs, $.bbl.	0.00	6.50
Total costs, $/bbl.	34.73	40.73
Net Income, $/bbl. feed	7.51	11.41

2.5.4 Hydro-visbreaking Process

There are two extension of visbreaking process which one of them in is one kind of non-catalytic processes, which is involves treatment with hydrogen at mild conditions and is completed in three reactors: (i) visbreaking; (ii) demetallization; and (iii) hydrocracking. The first reactor uses mild thermal process with hydrogen, the second one is for removing contaminants such as metals, prior to HCR. The last one may employ inexpensive catalyst (CoMo catalyst) to remove metals and for cracking of complex molecule respectively. The other one is Aqua-conversion (Hydro-visbreaking), which is a catalytic process using catalyst in slurry mode. This process was developed in 1996, UOP and Foster Wheeler-USA entered into a coalition with the research and technology support center of Venezuela's (PdVS AIntevep) Petroleum Organization. The alliance was to promote the commercialization and the on-going development of Intevep's noble Aqua-conversion process. In this process catalyst may be used as a support or mixed directly with the feedstock. The metals (metal salts) used for hydrovisbreaking are alkali metals such as potassium or sodium(Rana et al., 2007)

2.6 Hydro-treatment Categories

In general the hydro-processing technologies include fixed bed/moving bed/Ebullated reactors and their combinations of two or multiple options (Table 2.13).

Table 2.13: Hydro-processing Technologies (Ancheyta, Rana, et al., 2005)

Reactor type	Process	Licenser
Fixed bed	Continuous catalyst replacement (OCR)	Chevron Lumus Global (CLG)
	UFR, Up-flow reactor	Shell (Bunker flow)
		Axen (Swing reactor)
Ebullated bed	Hycon, Bunker type reactor	Shell
	Hyvahl, swing reactor concept	IFP (Axen)
	H-Oil	Axen (HRI/IFP): HRI (Hydrocarbon Research Institute)
	T-Star	Chevron
	LC-Fining	ABB Lummus
		Amoco oil (BP)
Slurry system	Microcat – RC	ExxonMobil
	Vebacombi-cracking	VebaOel
	Hydrocracking distillation (HDH)	Intevep
	Cash, Chevron activated slurry hydroprocessing	Chevron
	EST, Eni slurry technology	Eni Technologies
		Snamprogetti
	CanMet	Energy Research Laboratories, Canada

2.6.1 Fixed bed Process

The fixed-bed process technology is applied extensively and has the highest presence industrial applications due to its technical maturity, lower cost, stable and reliable performance in the world.

However, in order to prevent a too fast and uneconomic deactivation of hydroprocessing catalysts, the percentage of metals in the feedstock are strictly limited: (Ni+V)<250ppm(Rana et al., 2007). The major goal of fixed bed hydro-processing is hydro-treatment of heavy fractions with simultaneous HDS, HDN, HDM and asphaltene conversion. The hydrocracking activity remains moderate. This process can reduce the level of the impurities present in the feed and provide additional quantities of high quality feed-stocks for FCC and RFCC processes. In this process the conversion

increases with temperature, but due to the high coke deposition, it is not feasible to use at high temperature.

2.6.2 Moving bed Process

A major limitation of the fixed bed technology is that it can only handle feed with metal levels (Ni+V) <250 ppm. However, the refineries are faced with drastic changes in petroleum feed properties (such as increases in asphaltenes, sulphur, metals, and nitrogen contents) due to the growing volume of heavy crudes. To solve the problem, moving bed technology has been developed. Generally, the moving bed is usually used as the front reactor before the fixed bed to prolong the operating cycle. In the process, one or more moving bed reactors precede conventional fixed bed reactors, and its major goal is to remove contaminants which lead to plugging or fouling of the main reactors with periodic replacement of the catalyst and keep the main reactors online. Moving bed catalysts are similar to the fixed bed catalysts except that a catalyst shape is chosen which reduces abrasion and provides better particle strength. During the process, the catalyst bed slowly moves down the reactor as catalyst is withdrawn from the bottomand make-up catalyst added at the top. The back mixing of catalysts and feedstock is so slight that the efficiency of the process is higher than that of an Ebullated bed reactor, and the quality of products is better. On the whole, moving bed processing can handle a feedstock with metal content of up to 400 ppm and Conradson carbon residue (CCR) <20wt%. Nowadays, there are five commercial units worldwide in operation since the start-up of the first commercial unit was introduced in the 1990’s.

Three typical kinds of moving bed technology are reviewed in detail in the following: Chevron Lumus Global's on stream catalyst replacement (OCR) system, Shell's Bunker type reactor (Hycon) system and IFP's Hyvahl swing reactor system. (Liu et al., 2009).

2.6.3 Ebullated bed Process

As mentioned above, fixed-bed technologies have many problems in treating particularly heavy feeds with high heteroatom, metal and asphaltene contents. One solution to the problems is to use several fixed-bed reactors connected in series to achieve a relatively high conversion of such heavy feedstock, however, such designs would be costly, and for certain feedstock, commercially impractical. Therefore, Ebullated-bed technologies have been developed with numerous advantages in performance and efficiency, particularly with heavy crudes. In the process, the feed and H_2 mixture enters the bottom of the reactor and flows upward through a catalyst bed, expanding and back mixing the bed, minimizing bed plugging. The catalysts are not fixed and maintained in an ebullient or fluidized condition with up flowing feed. The reaction involves a three-phase system: gas, liquid and solid (catalyst) with good mass and heat transfer. The Ebullated bed process is able to convert most of the refractory heavy oil feedstock to either distillate products or low sulphur fuel oils. The most important feature of the Ebullated-bed process is its capability to periodically withdraw and add the catalyst to the reactor without interrupting operation. This is important for hydro-processing of high asphaltene and metal feeds. The bed design ensures ample free space between particles allowing entrained solids to pass through the bed without accumulation, plugging or increased pressure drop. This allows utilization of catalyst particles having a diameter smaller than 1 mm and results in a considerable increase of reaction rate. The process is flexible and can be operated either in a high conversion or low conversion mode. As far as the catalyst is concerned, catalysts used in the Ebullated bed are chemically similar to those used in the fixed bed and both are supported type catalysts. Such supported catalysts may be beads or extrudates containing small amounts of one or more active promoter metals such as cobalt, molybdenum or nickel deposited on an inert support material such as alumina or silica. There are a few

differences in the physical properties: Particle size, mechanical strength and shape. Ebullated-bed catalysts are made of pellets or grains that are 1-1.5 mm in size to facilitate suspension by the liquid phase in the reactor. The mechanical strength of the catalyst is even stronger than the fixed bed catalyst to sustain its operability (Reynolds, 2002). In general, there are two important Ebullated bed processes: the H-Oil process and the LC-Fining process.

2.6.3.1 H-Oil Process

This process was first commercialized in 1960s by HRI (Axen). The H-Oil Ebullated bed process can operate over a wide range of conversion levels and is particularly adapted to heavy vacuum residua with high metals and conradson carbon. Another major advantage of H-Oil is to maintain constant product properties during the cycle length. Since H-Oil reactor has the unique characteristic of stirred reactor type operation with a fluidized catalyst, it has the ability to handle exothermic reactions, solid containing feedstock and a flexible operation while changing feed-stocks or operating objectives such as the use of single- stage or two-stage processes.

The T-Star is an extension of H-Oil process and is another Ebullated bed process. T-Star units can maintain global conversions in the range of 20–60% and specifically HDS in the 93–99% range. The unit can act as either an FCCU pre-treated or VGO hydrocracker. H-Oil catalyst can be used in the T-Star process. A T-Star reactor can also be placed in-line with an H-Oil reactor to improve the quality of H-Oil distillate products such as virgin distillates, FCCU light or heavy cycle gas oil, and coker gas oils. In mild hydrocracking mode, the T-Star process can reach conversions up to the 60 vol.%. An advantage of operating the T-Star unit in mild hydrocracking mode is that the T-Star catalyst is not sensitive to sulphur and nitrogen levels in the feed and will provide constant conversion, product yields, and product quality. This consistency in

output is due to the reactor catalyst being replaced while the unit remains on-line. A commercial scale demonstration of the T-Star process in conjunction with the start -up of H-Oil units was done as a joint venture between Husky Oil, Canada and IFP(Scherzer & Gruia, 1996)

2.6.3.2 LC-Fining Process

The LC-Fining Ebullated bed process is a hydrogenation process which can be operated for HDS, HDM, and HCK of atmospheric and vacuum residues. LC-Fining is well suited for extra-heavy residue, bitumen and vacuum residue HDT feed-stocks and has demonstrated long cycle lengths. The general advantages of LC-Fining are: low investment, more light-ends recovery and lower operating costs. This process yields a full range of high quality distillates; heavy residue can be used as fuel oil, synthetic crude, or feedstock for a reside FCC, coker, visbreaker or solvent deasphalter. The LC-Fining process can achieve conversion for HDS of 60–90%, HDM of 50–98%, and CCR reduction of 35– 80%. Product quality is constantly maintained at a high level by sporadic catalyst addition and withdrawal. Reactor products flow to the high-pressure separator, low-pressure separator, and then to product fractionation. Recycled hydrogen is separated and purified. Process features include on-stream catalyst addition and withdrawal, thereby eliminating the need to shut down for catalyst replacement. The expanded bed reactors operate at near isothermal conditions without the need for quenches within the reactor. The reaction section uses a commercially proven low-pressure hydrogen recovery system. Separating the reactor effluent and purifying the recycled hydrogen at low pressure results in lower capital investment and allows design at lower gas rates. Operating conditions of Ebullated bed processes (H-Oil and LC-Fining) are summarized in Table 2.14. Ebullated bed processes can use extra-heavy feeds residues with elevated sulphur, nitrogen, and metals content (i.e. compared with

other crude oil distillation cuts) and do not require pretreatment prior to the Ebullated bed process. These processes have high liquid yield, however the conversion is not 100%. For any type of feedstock, high sulphur reduction is seen in all products with significant nitrogen reduction, but to a lesser degree than the sulphur.

Table 2.14: Some of the Ebullated bed Process and operating conditions

Parameter	H-Oil	LC-Fining
Temperature (C)	415–440	385–450
Pressure (MPa)	16.8–20.7	7.0–18.9
LHSV (h^{-1})	0.4–1.3	-
Catalyst (replacement rate (kg/ton feed))	0.3–2.0	-
Single train (throughput (BPSD))	up to 34,000	-
H2 use pie^3/b	1410	1350
Conversion (%)	45–90	40–97
HDS	55–92	60–90
HDM	65–90	50–98
Products (% w/w)		
C1–C4	3.5 C4=	2.35
C4–204 C	17.6 C5–177 C	12.6
204–371 C	22.1 177–371 C	30.6
371–565 C	34.0 371–550 C	21.5
C4>	22.8 550 C+	32.9

2.6.4 Slurry bed Process

Briefly, the slurry bed process is a hydrocracking process in the presence of catalysts and hydrogen at high pressure and temperature. The reaction involves mainly thermal cracking and the main goal is to convert residue into high value lighter distillates. The presence of catalyst and hydrogen restrains coke formation and leads to more stable products(Zhang et al., 2007). The slurry bed process shows its special superiority in treating heavy oils containing large amount of metals, carbon residue and asphaltene. Another feature of the process is its flexibility with respect to product selectivity and yield. On the whole, the slurry bed process as a residue processing technology has several advantages such as a more simple process flow scheme, flexible operation and process reliability, high space velocity and conversion rates, no bed plugging problems

and a wider adaptability to different sources of raw materials. The main disadvantage is that the operability is more difficult than for the other processes. In the process, the residue, finely dispersed catalyst or additive and hydrogen are mixed before being routed to the reactor. The reactants are well-mixed and kept in suspension and flow upward in the reactor. The product and catalyst are separated at the top of the reactor (high pressure high temperature separator). The coke formed during the reaction will deposit on the surface of catalyst and discharge from the reactor, thus there is no bed plugging problem. Solids particles are recovered with the unconverted organic fraction at the bottom of the separation section by distillation or by solvent deasphalting. To obtain better performances, some important parts including hydrogen distributor and internal loop reactor are used in the process. As discussed previously, the slurry bed process has the flexibility to produce, after severe hydrotreatment and/or hydrocracking to remove the heteroatoms and the olefinic and aromatic structure created in the process, gasoline, jet fuel, diesel fuel or vacuum gas oil to meet seasonal swings in product demand. Product yields depend on the extent of the conversion and to obtain high-quality products further processing is needed. Typical operating conditions in the reactor are temperatures of 420-460°C, a pressure of 10- 20MPa, LHSV 0.5-2.0 h^{-1} and single pass conversion of 70- 85%.(Zhonghuo et al., 2010).

2.7 Atmospheric Residue Desulfurization (ARDS) Process

Atmospheric Residual Desulfurization (ARDS) is another significant hydrogen-addition upgrading process, which is used mainly to upgrade low-value petroleum feeds to high-quality products of high commercial value and wider usability. This process is extensively used in upgrading of heavy petroleum oils and residues to more valuable clean environmentally friendly transportation fuels and to partially convert the residues to produce low-sulphur fuel oil and hydro-treated feed-stocks. Graded catalyst systems

in multiple reactors are used in the process in order to achieve HDS, HDM, HDN, and conversion of residues to distillates at desired levels. The characteristics of the feed-stocks processed in different reactors are significantly different. The quality of the feed entering the second reactor is strongly dependent on the operating severity in the first reactor and can have an important impact on the performance of the catalysts in the following reactor with regard to various conversions and deactivation rate.(Al-Nasser et al., 1996; Furimsky, 1998)

Unlike simple HDS processes, ARDS is a multitask process, where heavy petroleum feeds are hydro-treated and converted to light products that have lower boiling range, in comparison to the original feed. In an industrial ARDS process, low-value feeds are upgraded in the presence of hydrogen and several catalysts of different types grouped as one system. A typical ARDS catalyst system is usually a combination of at least three different types of hydro-treating catalysts, namely, HDM, HDS, and HDN with a considerable hydrocracking function. Many researchers have been done on this process in term on catalysts, operation conditions and modelling the kinetic reactions. (Marafi et al., 2006; Marafi et al., 2008; Haitham et al., 2011; Al-Mutairi & Marafi, 2012).

2.8 Combined Upgrading Process

It is in general accepted that light low-metal content feeds are better upgraded by RFCC, while heavy high-metal content feeds by hydrogen addition or carbon rejection type of technologies. For the case of heavy and extra heavy petroleum the decision of using coking or hydro-processing depends on technical and economical evaluations, not only based on the production of upgraded crude oil but also on the impact of the quality of the produced distillates on the performance of the down-stream refining processes, for instance distillates from coking base upgraded oil (coker naphtha and gas oil) require further hydro-treating, while those from hydro-processing may not need post-

treatment depending on the desired specification of final products. In any case, making a decision on which upgrading technology is more suitable for certain crude oil is not a simple task and must take into consideration several factors, among the most important are: price of crude oil, level of impurities of the feed, target of upgraded oil quality, and process scheme of the refinery where the upgraded oil will be sent. One attractive option to achieve the maximum benefit is by combining various technologies. That is, using more than one process to upgrade heavy petroleum. In such a way the advantages of each approach are put together in an integrated process scheme and this synergy may yield higher benefits than the use of single processes. The most promising combinations would be derived from solvent deasphalting, visbreaking, delayed coking, gasification, hydrocracking and hydro-treating. Some of them have been already reported and tested at commercial scale while others are still being proposed and under evaluation.

2.9 Review of Heavy Oil in Iran

Due to the current political climate in Iran as a one of the important oil-producing counties and the significant increases in global energy demand, National Iranian Oil Company (NIOC) policy is again focused on unconventional hydrocarbon resources for its potential to reduce future energy crises.

The largest heavy oil reservoirs in the Iran were found in the offshore section; with proven reserves of about 7 billion barrels Original Oil In Place (OOIP). Significant heavy oil deposits were also found in onshore, but data relating to these deposits is very sparse. Amongst them, production of SOROOSH reservoir, with API=19, was estimated 85,000 BPSD.

Upstream Processing

Unconventional oil deposits require upstream and downstream processing. Upstream processing refers to the extraction/production of the oil from the deposit. This oil is

typically extremely viscous and is composed of very high molecular weight compounds. Downstream processing, including upgrading and refining, produces marketable petroleum products.

Heavy oil has been produced in the Iran for over 80 years. Gas injection remains the most prominent production process for “common” heavy oil. Over the last ten years, steam and polymer injection as a new technologies, have been developed for heavy oil recovery projects and seems, are profitable by increasing the oil price. Nevertheless, project profitability is directly impacted by the energy source used for steam generation and by the cost of that source.

Recently, Water Alternating Gas (WAG) injection as a tertiary recovery method is one of the Enhanced Oil Recovery (EOR) methods which have recently received a great deal of attention in Iran.(Jafari et al., 2008)

Upgrading Heavy Oil Processing

Extra heavy oils from in Iran must be upgraded to a synthetic crude oil to be acceptable at many refineries that can only process light crude oils. Upgrading reduces the oil viscosity, increases the hydrogen to carbon ratio (H/C), reduces the molecular weight, and may significantly reduce or remove impurities that are problematic for most refineries. Since upgrading constitutes 90% of the downstream processing, a central facility that provides both upgrading and refining capacity could be economically viable depending on the location, the quality of the oil produced, the refining market at the time, available pipelines, energy sources (gas, coal, etc.) in the vicinity, the qualities of other crude oils being produced at the time, and a number of other factors. Partial upgrading renders the heavy oil/bitumen suitable for transportation via pipeline to a refinery for further downstream processing by reducing its viscosity and density.

Upstream upgrading crude oil, as feed is new strategy in Iran, however, hydrocracking processes and thermal cracking of VR, VGO or AR are favorable in Iran.

For example, thermal cracking of vacuum residues obtained from Iranian Tehran and Bandar Abbas refineries(Asgharzadeh et al., 2011)or hydrocracking of VGO obtained from Isomax distillation unit.(Sadighi et al., 2010)

2.10 Summary

Upgrading heavy oil into lighter fractions is crucial to satisfy the increasing energetic demands. The heaviest fraction, residue, contains most impurities, and so before converting, it becomes necessary to hydro-treat it. The impurities, present in large amounts, are mainly sulphur, nitrogen, oxygen and metals. Metals are poisons for catalysts in conversion units and sulphur content must be reduced to reach environmental constraints.

In this chapter we reviewed the most common and commercialized technology for upgrading heavy oil. This review included the technologies, reactors, process conditions, catalysts, feeds, conversion and the licensor of them. The technologies and conditions which were reviewed in this chapter are summarized in figures 2.4 and 2.5.

Figure2.6 summarizes the distribution of upgrading technologies and process capacity. Carbon rejection processes represent 56.6% of the total worldwide processing capacity mainly due to its relative low investment.

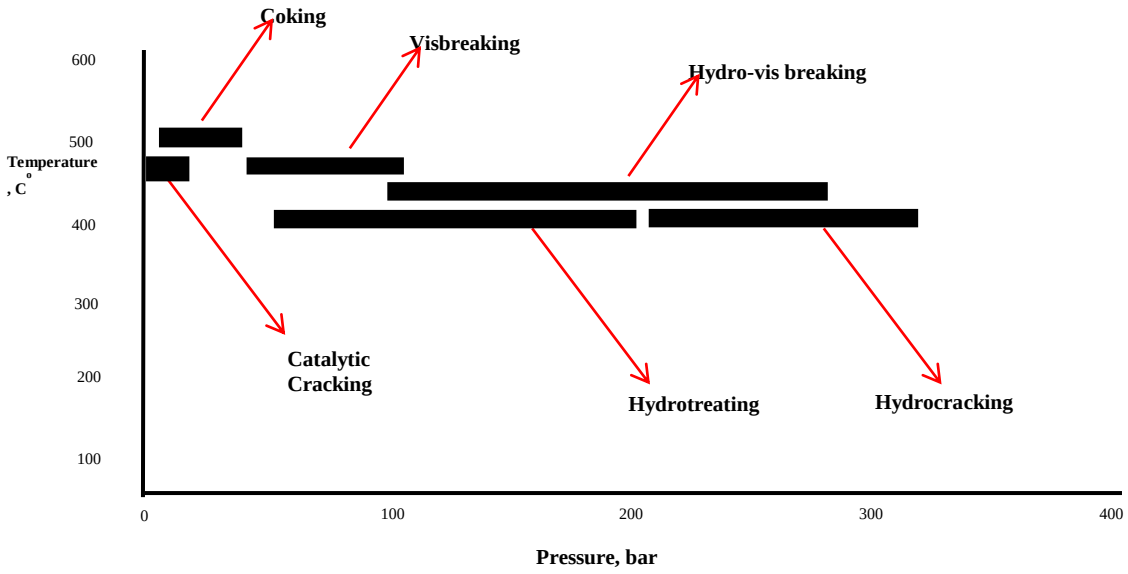

Figure 2.4: Temperature and pressure parameters for various processes (Speight, 2007)

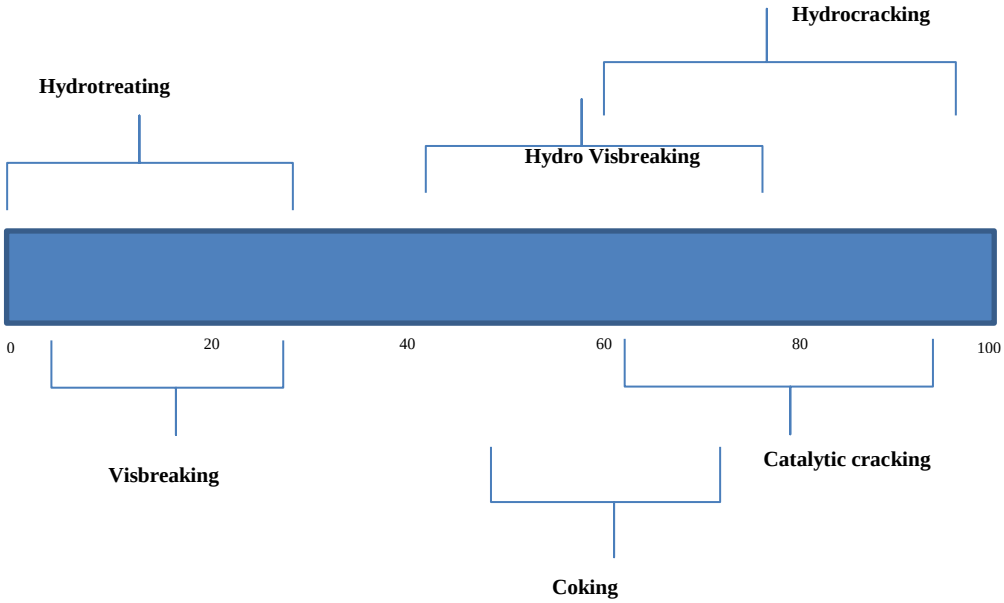

Figure 2.5:Feedstock conversion in various processes (Speight, 2007)

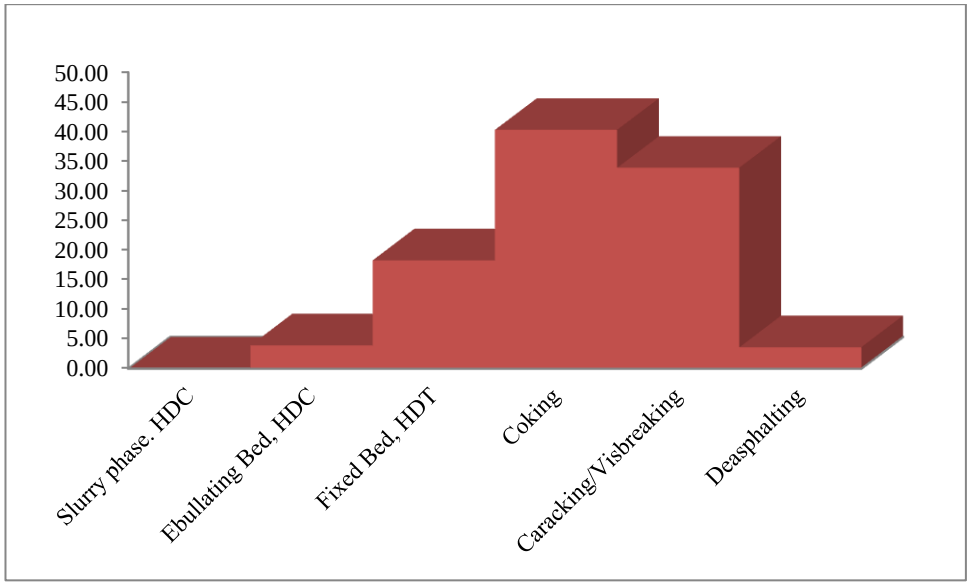

Figure 2.6: Worldwide distribution of commercial residue processing capacity
(Castañeda et al., 2014)

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Introduction

The design of any research program is of importance for a successful research study. Of course, there are other important factors which contribute to any successful research such as motivation and creativity of the researcher and the level of support. The purpose of this chapter is description of the research methodology which was used for conducting this thesis.

When considering possible ways of achieving the objective the designer will be constrained by many factors, which will narrow down the number of possible designs. There will rarely be just one possible solution to the problem, just one design. Several alternative ways of meeting the objective will normally be possible, even several best designs, depending on the nature of the constraints. (Towler & Sinnott, 2013). These constraints on the possible solutions to a problem in design arise in many ways such as shown in Figure 3.1.

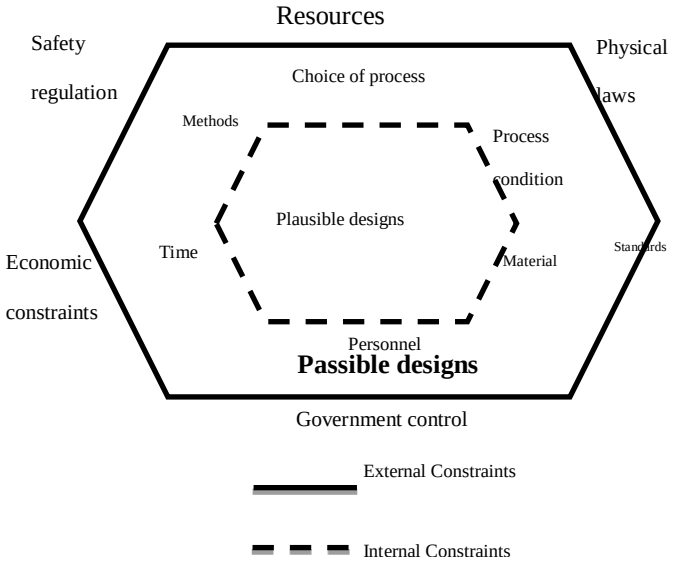

Figure 3.1: Design constraints (Towler & Sinnott, 2013)

Also considering the large number of design options resulting from the choice of the available technologies and the process integration options, a systematic process design method appears to be necessary. The uncertain nature of the design parameters thereby suggests an approach using multi-objective optimization in order to capture relationships between conflictive objectives. From engineering perspectives, understanding the links between decision variables and objective functions is also an issue.

In case of upgrading heavy and extra heavy oils, the decision of using technologies, conditions mostly depends on technical, economical evaluation and the impact of the quality of the products on performance of downstream refining process.

In any case, making the decision on which upgrading technology and condition are more suitable for certain crude oil is not simple task and must take into consideration several factors. Among the most important are following (Andersen & Speight, 2008)

- Price of crude oil
- Level of impurities of the feed
- Target of upgraded oil quality
- Process scheme of the refinery where the upgraded oil will be sent

In the past, for high metal content feeds, the traditional selection was a carbon rejection technology, particularly delayed coking. However for extra heavy oils it has been demonstrated that using coking technologies provokes the following adverse effects.(Trejo et al., 2010; Atkins et al., 2011)

- Low yield of upgraded oil
- High coke production
- Upgraded oil with high aromatics content
- Reduction of yield and quality of gasoline and diesel when refining
- Low upgraded oil value

To cover the range of properties of these “challenging crudes” the hydro-processing application has been extended, but differently to the traditional hydro-processing that works at high-severity reaction conditions, and hence at high conversion level, moderate hydro-treatment has emerged as another process option.

By several decades, the catalytic hydro-treatment process has been extensively used for upgrading different oil fractions. Naphtha is hydro-desulfurized to remove sulphur close to zero content; otherwise, the noble metal–based catalyst used in catalytic reforming is deactivated at very fast rate. Middle distillates are hydro-treated to reduce their contents of sulphur, nitrogen and aromatics to those values that allow meeting the current legislation in terms of environmental pollution. Among these distillates are straight-run kerosene and gas oil as well as other streams coming from secondary processes, such as light cycle oil from fluid catalytic cracking and coker gas oil. Heavier fractions (heavy straight-run gas oil and vacuum gas oils) need also to be hydro-treated before entering catalytic cracking units, by which apart from sulphur, nitrogen and aromatics, metals content is reduced. Finally, atmospheric and vacuum residua are either hydro-treated or hydrocracked aiming at reducing impurities content or lowering the molecular weight of the feed respectively. All these hydrogen addition operations are common in a typical refinery. However, the composition of the feed sent to refineries has become heavier in such an extent that for most of the cases, it cannot be processed without large changes, that is revamps of the plants or installation of new units capable to handle the new feed-stocks(Rana et al., 2008). This has been the turning point that has motivated the research of new alternatives to avoid major modifications of current refineries. One of the best approaches is the upgrading of the heavy petroleum before it enters the distillation column. To make this treatment economically attractive, the upgrading needs to be conducted at moderate reaction conditions, if not,

the well-known high investment of hydro-treatment is not compensated by the increase in distillates yield and quality.

The reactor type and configuration, reaction conditions and catalyst properties are defined according to the type of feed to be treated. For naphtha fraction, low-severity reaction conditions and a simple fixed-bed two-phase (gas and solid catalyst) reactor is required, whereas for heavy oil, depending on the desired objective, the feed can be hydro-treated in single or in series trickle-bed reactors(Ancheyta et al., 2002) or hydrocracked in moving or Ebullated-bed reactors. In any case, the extent of reactions occurring can vary significantly; for instance, during hydro-treatment of heavy oil, hydro-desulfurization and hydro-demetallization are the most relevant reactions without appreciable change of molecular weight of the feed, while during hydrocracking (HDC) of heavy oil, high conversion of the residue fraction is observed.

The main objective of this study is finding the optimum process conditions for upgrading Iranian heavy oil.

3.2 Upgrading heavy oil Process modeling

Process modeling is an essential tool in order to understand and to analyze the various steps of experimentation, data analysis, process development, and engineering design during all systematic investigation. This tool provides support for the planning, design, and evaluation of systems as well as the evaluation of strategies for system transformation and change.

Modeling has drawn the attention of scientists and engineers for many decades and now is still a subject of major importance for the knowledge of unitary processes as a fundamental key in process design and scale up. There is a wide range of possible reasons for undertaking a modeling and simulation study (Louis & Arbez, 2007; Towler & Sinnott, 2013). Data is always easier to obtain from a model than from the system

itself in most time and this is another important reason for supporting experimentation with a model. Furthermore, the fact that the platform for the modeling is a computer and this ensures reproducibility of results which is an essential requirement for establishing credibility of any investigations. The goal of a process simulation in systems is to find optimal conditions for an examined process. This is essentially an optimization problem which has to be solved in an iterative process.

3.2.1 Hydro-treatment Variables

The efficiency of the hydro-desulfurization process is measured by the degree of sulfur removal or, in other words, by the yields of sulfur-free products. However, there are several process variables that need special attention as any one of these variables can have a significant influence on the duration and effectiveness of the hydro-desulfurization process. The major process variables are: reaction temperature, hydrogen to oil ratio, reactor pressure (hydrogen partial pressure) and liquid hourly space velocity.

The primary reaction variables are reactor temperature, pressure, space velocity, hydrogen consumption, nitrogen content of the feed, and hydrogen sulfide content of the gases.

Reactor temperature is the primary means of conversion control. As the catalyst ages it is necessary to raise the average temperature to compensate for the loss in catalyst activity (0.1°F/day) (Gary & Handwerk, 1984). Temperature control is achieved by injecting cold hydrogen between the adjacent catalyst beds. The primary effect of reactor pressure is through the partial pressures of hydrogen and ammonia. An increase in total pressure increases the partial pressures of both hydrogen and ammonia. Conversion increases with increasing hydrogen partial pressure and decreases with ammonia partial pressure. The hydrogen effect is greater, however, and the net effect of

raising the total pressure is to increase conversion. The space velocity, generally reported as Liquid Hourly Space Velocity (LHSV), is the ratio of the liquid volumetric flow rate to catalyst volume. The catalyst volume is constant; therefore, the space velocity varies directly with feed rate. As the feed rate increases, the time of the catalyst contact for a given volume of feed is decreased and conversion is lowered. In order to maintain conversion at the proper level, when the feed rate is increased, it is necessary to increase the temperature.(Govindhakannan, 2003)

3.2.1.1 Temperature

Rates of all reactions in hydrocracking increase with increasing temperature. Increasing temperature will increase hydrogenation but hastens the deterioration in the number of active catalyst sites. Through the run, temperature control is used to offset the decline in catalyst activity. The maximum temperature is usually limited by process equipment design where most hydrocracking reactors have a metallurgical limit of some 800°F. Except for very high, pressure hydrogen operations, coke deactivation due to thermal cracking would prohibit operation above 800°F in any case. There will be some temperature rise across the catalyst bed due to the overall exothermic nature within the hydrocracking reactor.

3.2.1.2 Pressure

Reactor pressures in hydrocracking vary depending on the requirements of the feed. Increasing pressure increases hydrogen partial pressure and retards coking deactivation. This is of greater concern with heavier stocks, higher con-carbon stocks and cracked or coked stocks. Both sulfur and nitrogen removal is aided by higher hydrogen pressure. Aromatics saturation is highly correlated with hydrogen pressure.

3.2.1.3 Liquid Hourly Space Velocity (LHSV)

Liquid hourly space velocity (LHSV) is defined as volume of oil per volume of catalyst per hour. As used in refinery operations it is normally calculated as cubic feet of oil per cubic foot of catalyst per hour. In all hydrocracking reactions and increase in LHSV (oil feed rate) results in decreases in desulfurization, aromatic saturation and other hydrogenation reactions.

A summary of the experimental rigs in batch and semi-batch mode for studying the hydro-treating of heavy oil is presented in Table 3.1.

Table 3.1: Effect of different heavy feed-stocks on the deactivation of a commercial hydro-treating catalyst (Centeno et al., 2012)

Author	Type of feed	Type of reactor	Reaction conditions	Type of catalyst	Main findings
(Nuñez et al., 2000)	Deasphalted vacuum bottoms	Two fixed-bed industrial reactors	T_{max} = 400 °C, P = 103.4 bar, LHSV = 1.0 h^{-1}, T-O-S = 241 days	Six Ni-Mo/Al_2O_3 catalysts with different content of Mo and Ni	Deactivation of catalysts depends on chemical properties of the feed, pore structure, active metal loading, surface area and pellet size of the catalyst, as well as position along the packed-bed reactor, Dominant deactivation by metals at the upper part of the first reactor
(Callejas et al., 2001)	Residue from Maya crude	Trickle-bed reactor	P H_2 = 100 bar, LHSV = 1.1/h g cat, H2/oil ratio = 0.2 kg/kg, T = 375 °C	NiMo/Ɣ-Al2O3 HDM catalyst	Vanadium deposition becomes more diffusion rate limited, resulting in a less deep penetration into the catalyst pellet
(Higashi et al., 2002)	Heavy residue with high asphaltene content	Fixed-bed reactor	T_{max} = 400 °C, P = 108 bar, LHSV = 1.0 h^{-1}, T-O-S = 241 days	38/31/31 vol.% HDM/NiO-CoO-MoO_3/NiO-MoO_3 catalysts	Catalyst activity strongly damaged with low H_2/HC ratio and low hydrogen pressure
(Marafi et al., 2003)	Kuwait AR, HDM residue, HDM/HDS residue	Fixed-bed reactor systems	T = 360-380°C, 390°C P=120 bar, LHSV = 0.32 and 2.0 h^{-1}, H_2/CH = 570 mL/mL and 680 mL/mL	Three catalyst: Cat A: HDM Cat B: HDS Cat C: HDS/HDN	Proper selection of feedstocks is crucial to study the performance and screening of candidate catalysts for graded catalyst systems
(Hauser et al., 2005)	Kuwait AR	Fixed-bed reactor	T = 380°C, PH_2 = 120 bar, LHSV = 1 h^{-1}, H_2/Oil ratio = 570 mL/mL, T-O-S = 1-240 h	Mo/Al2O3 HDM catalyst	Initial coke formation was described in terms of its chemical composition and structural alterations as a function of T-O-S
(Marafi et al., 2007)	Kuwait AR	Fixed-bed single micro-reactor	T = 380 °C,P = 120 bar, LHSV = 1.0 h^{-1}, H_2/CH= 680 mL/mL, T-O-S = 120 h	Three catalyst: Mo/Al_2O_3Ni-Mo/Al_2O_3Ni-MoP/Al_2O_3	Physical-chemical properties of the catalysts have a strong influence on catalyst deactivation by coke and metal deposition
(Almutairi et al., 2007)	AR from Kuwait export crude and Eocene crude	Two fixed-bed reactors in series	T= 370-412 °C, P=120 bar, LHSV=2.0h^{-1}, T-O-S = 3800 and 7500 h	Five catalysts: 2 HDM catalysts and 3 highly active NiMo HDS catalysts	Main reason for the difference in performance of catalyst system attributed to content and composition of asphaltenes in the feed-stocks

3.3 Overview of Multi-objective Optimization

Day-to-day decision making requires both objective and subjective perspectives, utilizing the former for rational, constrained modeling and the latter for adapting specific problem issues to the decision-making process.

A decision support system (DSS) is defined as a software-based tool assisting in the decision-making process by interacting with both internal/external users and databases while utilizing standardized or specific algorithms for problem solving(Fjermestad, 2009).

Power, (2008) identified four main types of DSSs, depending on the main drivers guiding the decisional process:

-Model-driven DSSs: such DSSs require a limited amount of data because of the intrinsic composition of the system, used to evaluate quantitative data in a tailor-made structure that can be adapted to other external requirements. Initially developed for financial planning, this category of DSS was later used for multi-criteria decision making and spatially driven decisions such as logistics or distribution modeling.

-Data-driven DSSs: the database structure behind the DSS is emphasized, and the operations of data-warehousing and manipulation are the most relevant for such DSSs. Online – meaning interactive (such as the OLAP) – and offline applications can be found, and web-based data-driven DSSs currently represent the natural evolutions of such models.

-Communication-driven DSSs are used for exploiting the network and communicating capabilities of the system, which includes the use of groupware, conferencing or other computer-based communications. This category is directly related to group DSSs, developed to promote a participatory approach to the decision process, and their relation with model-driven DSSs has been studied, aiming to include the shared approach of the former with the structured modeling of the latter.

-Document-driven DSSs, also called “text-oriented DSSs”, are used for document retrieval, especially in large groups/organizations, to support the decision-making process. The advent of a Web-based system increased the possibility of such DSSs, allowing rapid access of documents distributed in worldwide databases.

-Knowledge-driven DSSs: these are specific, tailor-made systems used in a particular domain and developed for a particular person or group of people. Power (Power, 2008) acknowledged the relationship with Artificial Intelligence systems, in which the DSS follows a series of rules to evaluate and eventually make decisions on the problem to be analyzed.

Arnott& Pervan (2005) reported a framework for DSS classification and sub-classification, identifying personal DSSs, group support systems, executive information systems, intelligent DSSs and knowledge-management-based DSSs. Each of such DSSs presents sub-branches depending on their specific features and temporal evolution. In particular, model-driven DSS represents the focus of this study. The modeling stage, focusing on multi-criteria modeling, will be investigated in the following paragraphs.

Multi-criteria, multi-attribute and multi-objective analyses – while similar in their ultimate purpose of assisting with the final decision-making process (Geldermann et al., 2008) differ in their defining concepts. Multi-criteria decision-making (MCDM) deals with a general class of problems that involves multiple attributes, objectives and goals. Although MCDM represents the major class in decision-making support systems, multi-attribute (MA) and multi-objective decision-making (MODM) represent their subclasses, related to more specific approaches in the decision-making model. Life cycle assessment (LCA) and impact assessment (IA) are tools used in industrial ecology to quantify and evaluate the emissions (air, water and soil) from various parts of a production process and then evaluate their impacts on different elements of the

ecological system (e.g., human health, ecosystem damage and resources) depending on the IA methodology chosen.

Optimization with multiple conflicting objectives has no single best solution, but a set of solutions, named the "Pareto-set" for Villfred Pareto (1848–1923), who first studied them, which can be applied to social science, economy and game theory. Multi-objective optimization techniques therefore identify a set of non-dominated solutions which represent the optimums for a given problem. The concept of domination can be illustrated as follows: an alternative is non-dominated by b if is better than b for at least one objective while not being worse than b for all of them.

Identifying the Pareto-frontier means also satisfying the following requisites for the solutions identified while minimizing the total elaboration time, as reported in (Rodriguez et al., 2010):

•Spread: To find a set of solutions that "capture the whole spectrum" of the true Pareto front;

•Accuracy: To find a set of solutions as close to the real Pareto front as possible;

•Diversity: To find a set of solutions as diverse as possible.

According to (Weise, 2009), the five main stages of evolutionary algorithms involve the following:

•Initial population, which allows the initial sample for analysis to be created from the possible set of candidate solutions;

•Design evaluation, which computes the objective value from the candidate solution;

•Fitness assignment, which, depending on the objective, determines the fitness of the candidate solution relative to a fitness criterion (weighed sum of objective values, Pareto ranking, etc.) which evaluates the suitability of the candidates to the optimization required;

•Selection: based on the fitness of the candidate solution, at this stage the population (the group of candidate solutions) to be maintained is selected, while the remaining solutions are discarded.

•Reproduction: selected candidate solutions are reproduced by different mechanisms such as partial mutation, crossovers, or complete change.

As a class of MO techniques, the family of evolutionary algorithms includes, among others, evolution strategies (ES), genetic algorithms (GA), genetic programming (GP) and learning classifier systems (LCS) (Weise, 2009). Among GA techniques, the non-dominated sorting algorithm (NSGA) represents an increasingly used method for the design stage. NSGA and its variant NSGA-II, first developed by Srinivas& Deb (1994), are population-based meta-heuristics encompassing seven steps for design optimization (Weise, 2009), i.e., population initialization, non-dominated sorting, crowding distance, selection, genetic operators, recombination and selection. Having defined the initial population based on problem constraints or user design of experiments (DOE), sorting is performed by assigning a priority value ("rank") to non-dominated designs, selecting designs for further explorations based on rank and crowding distance, i.e., higher fitness is assigned to individuals located on a sparsely populated part of the front (Murugan et al., 2009). Genetic operators, mainly "recombination", "crossover" and "mutation", are used for exploring the design space, which is then selected, maintaining a range of best-performing designs ("elitism") for the next fitness assessment, until the last generation of designs is assessed or the end criterion is reached.

To overcome the shortenings of lateral diversity in Pareto front determination of NSGA-II, Jeyadevi et al. (2011) developed a modified NSGA (MNSGA-II) including a controlled version of elitism for improving the exploration stage and the lateral distribution of the Pareto Front, used in reactive power dispatch modelling. Guo et al. (2013) used a modified version of NSGA-II to solve scheduling issues in production

planning, relating scheduler utilization to a production process simulator. Panda (2013) used NSGA-II for electrical noise reduction in controller designs.

Yusoff et al. (2011) reviewed the application of NSGA-II in machining design, concluding that such an algorithm represents a reliable and popular tool in MO machining setup, allowing the inclusion of multiple performances and variables. There are numerous published applications of MCDM in plant design. Multi-objective (MO) analysis has been broadly used in designing product components, but limited research has considered the environmental impacts of the process. Vince et al. (2008) assessed the design installation of a Reverse Osmosis plant for desalinated water production, including both economic and environmental criteria. However, in this analysis, the environmental impact was limited to a quantitative environmental assessment of water discharges, considering electricity production and the water recovery rate as the environmental criteria. Mirzaesmaeeli et al. (2010) treated environmental emissions as a constraint in a mixed integer linear programming (MILP) optimization of a Canadian power producer, while the optimization model proposed in (Rong & Lahdelma, 2007) included environmental emissions considered as externalities, i.e., those externally generated but unaccounted for in the costs. Harkin et al. (2012) used MO optimization to design CO_2 capture systems retrofitted in coal power stations. They took into account the percentage of CO_2captured (maximized) and the energy input to the process (minimized), evaluating results as a function of the input parameters. Guillén-Gosálbez (2011) applied MO optimization, discussing its validity when assessing multiple objectives such as environmental outcomes, and introduced a mixed MILP-MO model, which they then applied to heat exchanger designs and petro-chemical supply chains. Environmental impacts within LCA typically include acidification, eutrophication, global warming and eco-toxicity. Bernier et al., (2010) used both thermo-economic and environmental objectives for a carbon dioxide capture plant design, integrating LCA (in

terms of global warming potential) into the optimization model. Applied evolutionary algorithms were used in (Dipama et al., 2010) for power plant capacity estimation, considering only technical (Maximize Exergy efficiency) and economic (minimizing total costs) criteria in identifying Pareto-optimal solutions.

Mattiussi, et al. (2014), presented a framework for an energy supply decision support system (DSS) for sustainable plant design and production. They used multi-objective and multi-attribute decision-making (MODM, MADM) modeling together with Impact Assessment (IA) of the emission outputs.

STAGES	OBJECTIVE	TOOLS	DONE BY
DOE-Initial Set of Variables	Define the initial generation of candidate solutions to be assessed	DOE Algorithms	Mode Frontier/ User
Output Calculation	Calculate the results from the single simulation of each generation of candidate solutions	Mathematical Model	Microsoft Excel
Scheduling	Variants the candidates solutions depending on simulation results	Scheduling Algorithm	Mode Frontier
Pareto Front	Identifies the non-dominated solutions	Optimizer	Mode Frontier

Figure 3.2: Shows the Optimization procedure in Multi-objective decision-making process.
(Mattiussi et al., 2014)

Areas of application of multi-objective optimization include the design of chemical plants(Chakraborty & Linninger, 2002; Guillén-Gosálbez et al., 2008); the design and scheduling of batch processes(Stefanis et al., 1997;Cavin et al., 2004); the design of utility systems (Chang & Hwang, 1996; Papandreou & Shang, 2008); the design and planning of chemical supply chains(Hugo & Pistikopoulos, 2003; Puigjaner & Guillén-Gosálbez, 2008; Bojarski et al., 2009; Guillén-Gosálbez & Grossmann, 2009; Guillén-

Gosálbez & Grossmann, 2010); and the strategic planning of hydrogen supply chains(Hugo et al., 2005; Guillén-Gosálbez et al., 2010), among others.

A typical multi-objective optimization problem can be formulated as: Equation 3.1

$$\text{Min } f_m(x) \qquad \text{Equation 3.1}$$

$$\text{Subject to } x \in S$$

Where m ($m \geq 2$) is the number of objectives; $f_i(\mathbf{x})$ is the i^{th} objective function; $x=(x_1, x_2, ..., x_n)$ is the decision variable vector, where n is the number of decision variables; i is the index of the decision variables; j is the index of the objectives; and $\boldsymbol{S}$ refers to the feasible solution space which is defined by the constraints. Different problems have different sets of constraints. Here $\boldsymbol{S}$ is used for a general notation only of the feasible solution space defined by the constraints functions. In practice, some objectives could be in the maximization form, but they can be easily transformed to a minimization form or they can keep their maximization form in the optimization process. In order to simplify the notation, it is herein assumed that all the objectives are in the minimization form, for the purpose of illustration of the concepts. In multi-objective optimization, the solutions are always vectors that have several objectives. Thus, the concept of dominance is typically used to compare different solutions.

Dominance: In the problem of Formulation 3.1, a solution $x^1$with the objective vector $f^1= (f^1_1(x^1), f^1_2(x^1),\ldots, f^1_m(x^1))$ dominates another solution $x^2$with the objective vector $f^2= (f^2_1(x^2), f^2_2(x^2),\ldots, f^2_m(x^2))$ if and only if $f^1_j(x^1) \leq f^2_j(x^2)$,, all $j = 1, \ldots, m$ and $f^1_j(x^1) < f^2_j(x^2)$for at least one index j. (Nakayama et al., 2009).

Multi-objective optimization provides as output a set of Pareto optimal alternatives that feature the property that it is not possible to find another feasible solution that is better in one of the objectives without necessarily worsening at least one of the others. One of its main advantages is that it allows articulating the decision makers 'preferences

in the post-optimal analysis of the solutions found. This makes it possible to identify solutions that achieve large environmental improvements at a marginal increase in the cost.

In a multi-objective optimization problem with all the objectives that are to be minimized, a Pareto solution can be defined as: for a feasible solution, if there is no such a feasible solution **x** that for all objectives:

$$f_j(x) \leq f_j(x^*) \quad (j=1,2,\ldots,m)$$

and that at least for one objective $f_j(x)<f_j(x^*)$then **x***is called a Pareto solution. In short, if a feasible solution x*is not dominated by any other feasible solution, then it is a Pareto solution: for a feasible solution x*, if there is no such a feasible solution x that for all objectives.

$$f_j(x) <f_j(x^*) \quad (j=1,2,\ldots,m)$$

Then x* is called a weak Pareto solution.

It is worth mentioning that there are two classes of Pareto solutions: properly Pareto solutions and improperly Pareto solutions. Improperly Pareto optimal solutions are those that allow infinite or large enough trade-offs between the solutions. In transportation asset management, most performance measures or objectives have a range, and therefore infinite trade-offs between the solutions do not exist. Thus, the "Pareto solutions" in this dissertation refers to properly Pareto optimal solutions. The set of all Pareto solutions is called Pareto frontier(Nakayama et al., 2009). Thus, each solution on the Pareto frontier is not dominated by any other feasible solution. Pareto frontiers are very important to decision-makers in conducting analysis and to examining their real preference structure. An example of a Pareto frontier is presented in Figure 3.3. The points in the figure represent all feasible solutions of a bi-objective optimization problem that attempts to minimize both objective $f_1$and objective f_2. Each point represents a feasible solution. It is seen that solutions on the curve are not

dominated by any other solution; these solutions comprise the Pareto frontier of the bi-objective optimization problem. All other solutions that are not on Pareto frontier are dominated by at least one of those solutions on the Pareto frontier.

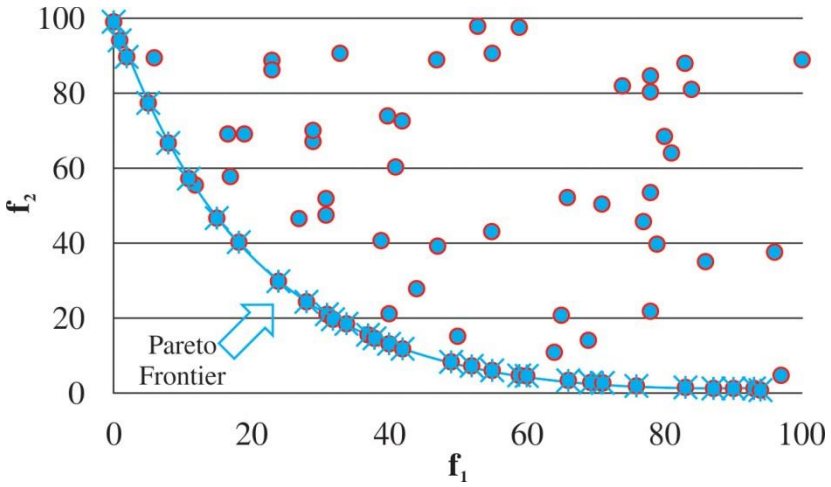

Figure 3.3: An Example of Pareto Solutions and a Pareto Frontier (Nakayama et al., 2009)

It is worth mentioning that, in the optimization problem with more than two objectives, the Pareto frontier maybe a hyper plane, not a two-dimensional curve. For instance, Figure 3.3 presents a three-dimension surface which is the Pareto frontier of a triple-objective optimization problem.

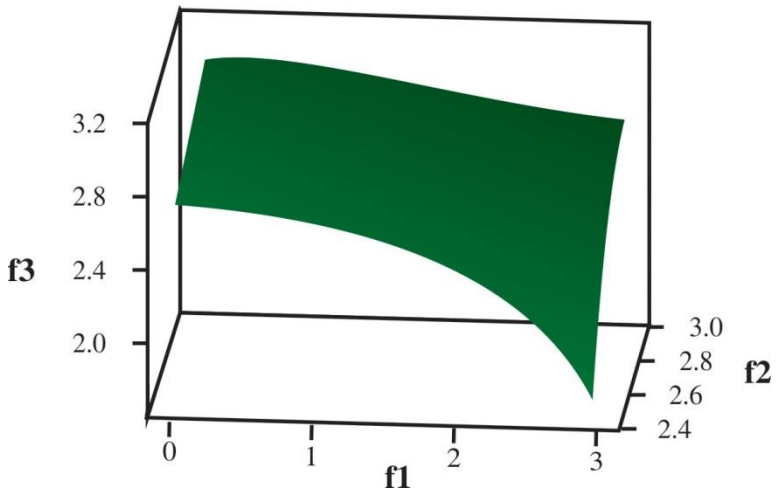

Figure 3.4: An Example of Pareto Frontier Surface for Three Objectives (Alarcon-Rodriguez et al., 2010)

There are several ways of classifying multi-objective optimization approaches and methods.

3.4 Artificial Neural Network (ANN)

An artificial neural network is a flexible mathematical model which imitates the working principles of human brain. Three elements are particularly important in any model of artificial neural networks: the structure of the nodes, the topology of the network and the learning algorithm used to find the weights of the network (Rojas, 1996). The ANN is composed of many nodes that operate in parallel and communicate with each other through connecting weights. In terms of their topology structures, neural networks can be divided into two types: feed-forward networks and recurrent networks. There are two types of learning algorithm used in neural networks: supervised and unsupervised learning. The ANN can realize complex nonlinear mapping by using learning algorithm to adjust the connection weights based on its distributed structure. ANN can discover patterns adaptively from the data. The ANN is capable of learning complex relationships from many individual examples (or experiences). In addition, they have fault and noise tolerance. In addition, the ANN has high robustness and generalization capability. They have been used with success for prediction.

Over the last few decades the use of artificial neural networks (ANNs) has increased to cover a broad range of areas including engineering, economic and medical sectors. There have also been significant developments in the ANN model reduction techniques to improve the computational efficiency especially when large and complex structures are required to approximate and capture highly nonlinear models. One of the benefits of model reduction is avoiding the over fitting of the networks and therefore ensuring the ANN's ability to accurately predict data outside of its training dataset. Development of new approaches and algorithms has led to a number of methods which are able to compete with each other in terms of reduction capabilities as well as model accuracy.

An ANN hybrid model was used by Bollas et al., (2003) to scale up a FCC pilot plant into an industrial scale plant. The pilot model was able to predict the weight percent

conversion and the coke yield. The hybrid model was then compared with the pilot model and the pure ANN model. The results showed that the hybrid model has better extrapolation capacity.

Bellos et al, (2005) used a hybrid ANN model for hydrodesulphurization reactor modeling. They coupled the deterministic model which was used to study the reactor performance and hydrogen consumption, with an ANN model which was able to evaluate the kinetic parameters. The obtained results showed that the hybrid model was capable of predicting the reactor performance.

The crude oil description using the near infrared spectroscopy was performed by Falla et al, (2006). This analysis was called Sim-Dis (Simulation Distillation) and was faster than the true boiling point method. Forty oil samples with API of 1.31-36.4 were gathered. The ANN was applied, which generated the Sim-Dis curves accurately.

An ANN model was used by Zahedi et al,(Zahedi et al., 2006) for simulation of an industrial Hydro-treated Unit. They used Radial Basis Function (RBF) modeling as an optimum architecture to predict hydrogen demand, outlet API, and sulphur weight percent as a function of inlet API and sulphur weight percent for seven different feed stocks. A comparison between their models with the obtained results of a conventional simulator confirmed the superiority of the ANN model.

In another study they focused on enhancing the gasoline production of an industrial catalytic reformer unit. The ANN model anticipated the unit outputs accurately and led to 2.38% increase in gasoline production yield(Zahedi et al., 2008).

Aminian & Shahhosseini (2008) used ANN to predict the fouling behavior of a crude oil preheat heat exchangers. They also used sensitivity analysis known as the “sequential zeroing of weights” to determine the effects of various parameters on fouling. Design of the expert system for an industrial distillation column using NN and its optimization using genetic algorithm was performed by Motlaghi Jalali &Nili

Ahmadabadi (2008). They used the operating conditions and the product quality as ANN input and outputs respectively. Then, the oil production cost function was minimized.

In another attempt delayed coking unit was also modeled by Zahedi et al, (2009).They used both MLP and RBF NNs. The obtained results showed that the generalization capability of the RBF network in modeling of this unit was better than the MLP.

Recently o research group have successfully employed ANN in sour gas water content estimation and also efficiency of sieve trays in distillation column (Shirvany et al., 2010; Zahedi et al., 2010).

The number of hidden layers and the number of nodes in each layer depends on the complexity of the patterns and the nature of the problem to be solved. The use of a single hidden layer is sufficient to approximate to any continuous function as closely as requested(Hornik et al., 1990) and the study also shows that having more than three layers may not result in significant performance improvements (Patuwo et al., 1993).

A typical ANN formulation relies on solving the following non-linear programming (NLP) problem:

$$Min_{a,b,w,h,W,B,u} E_1 = \sum_{k=1}^{N_o} (u_k^{\sim} - u_k)^2 \qquad \text{Equation 3.2}$$

(ANN Prediction Error Objective Function)

Subject to: Equation 3.3

$$a_j^1 = \sum_{i=1}^{N_x} w_{ji}^1 x_i + b_j^1,$$
$$j=1,\ldots,N_n$$

(Activation Variables of the First Hidden Layer)

$$h_j^1 = \tanh(a_j^l) j=1,\ldots,N_h$$ Equation 3.4

(Nonlinear Transformation of Activation Variables)

$$a_j^l = \sum_{i=1}^{N_n} w_{ji}^l b_j^{l-1} + b_j^1,$$ Equation 3.5
$$j=1,\ldots,N_n \quad l=2,\ldots, N_h$$

(Activation Variables of the Remaining Hidden Layers)

$$u_k = \sum_{i=1}^{N_n} W_{ki} h_j^{N_h} + B_k k=1,\ldots..,N_o$$ Equation 3.6

(ANN Output)

where x_i denotes the input values to the network, $i = 1, \ldots, N_x$ is the number of inputs, N_n linear combinations of these inputs gives the activation variables, a_j^1, where N_n is the number of nodes in the hidden layer, the equation 3.6 denotes the index of the first hidden layer, w_{ji} are the weights and b_j the biases. These activation variables are then transformed non-linearly to provide h_j^l, the output of a hidden layer; note that non-linear transformations other than $\tan_h$ are also used in the literature. h_j^l, the output of a hidden layer then becomes the input to next hidden layer. The outputs from the last hidden layer, h_j^{Nh}, are then combined to provide the outputs, u_k. N_o is the number of nodes in the output layer and W_{ki} and B_k are the weights and biases, respectively. Let $\hat{u}_k$ denote the desired output, the training of the network can then be formulated as

minimization of the error function, E_1. For simplicity in presentation, u_k, $\hat{u}_k$, a_j^1, h_j^1 and x_i represent vectors for all the points in the training data set.(Figure 3.5)

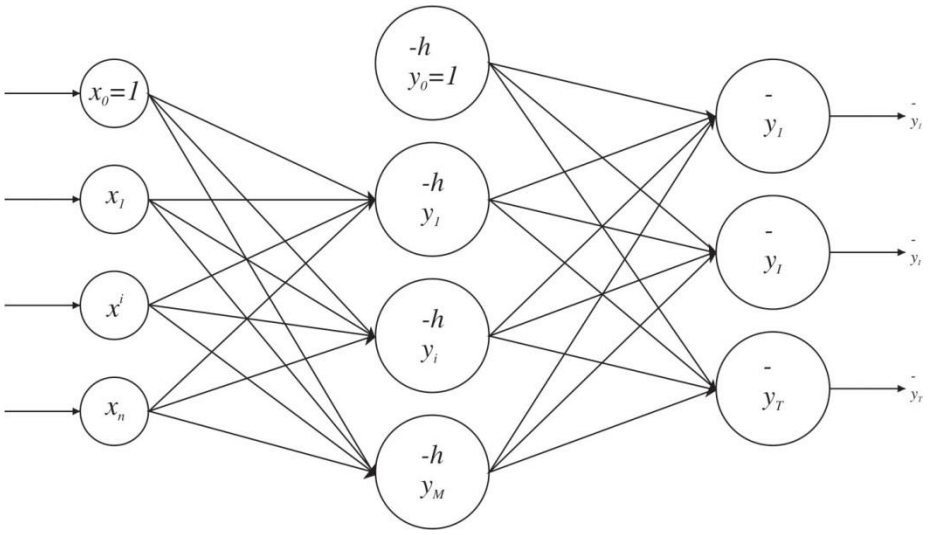

Figure 3.5: Architecture of a feed forward neural network

3.5 Optimization in Upgrading Heavy Oil Processes

The principal operating variables in hydro-treating are temperature, hydrogen partial pressure (H_2pp), and liquid space velocity (LHSV)(Speight, 2000; Gary et al., 2007)

Changing operating conditions in upgrading processes may influence the performance and consumption of hydrogen. For example, changes in composition of feedstock, operating temperature, and pressure result in varying conversion of reactions. Consequently, the hydrogen consumption, flow rate, and purity of recycle and purge streams of hydrogen consuming processes may also change.

One of the complex problems for the control in which a computational intelligent approach is amenable is a crude oil upgrading processes. In these processes, the first objective is to perform an entire process optimization including high production rate with a required product quality by searching for an optimal operating condition of the operating variables (Frenkel, 2011; Ouattara et al., 2012). In the previous decade, there was considerable research concerning the optimization of crude distillation

processes(Ghashghaee & Karimzadeh, 2011). Seo, Oh, and Lee (2000), the optimal feed location on both the main column and stabilizer is obtained by solving rigorous "a priori" models and mixed integer nonlinear programming. The sensitivity to small variations in feed composition is studied in Dave (2003). Julka et al. propose in a two-part paper(Julka et al., 2002) a unified framework for modeling, monitoring and management of supply chain from crude selection and purchase to crude refining.

Biscarri et al, (2012), concerned platforming unit as a part of the crude oil distillation and focused on heat recovery, 80% of the energy consumption (67% of the energy invoicing tasks) corresponds to the fuel consumption in the boilers of the previous task (the reaction unit) not only the production rate of the distillation unit(Iranshahi et al., 2011; Meidanshahi et al., 2011)

At present, research is not only focused in the rise of the production rate but also in making customized products (Frenkel, 2011) and in the improvement of product quality(Rahimpour et al., 2011). Nonlinear state estimation research (Jana et al., 2009) and optimal planning strategy research (Kuo & Chang, 2008) are available. The main objective of these papers was to remove impurities in the distillate and maintain the minimum possible amount of product (butane) in the bottom residual fuel oil to maximize the yield of the product.

The energy management (De Lima & Schaeffer, 2011) and the energy efficiency(Chiwewe & Hancke, 2012) become important problems. The objective is to perform a complete plant energy process optimization, including an adequate production rate with the required product quality while minimizing operating costs (fuel consumption in boilers) through a data mining approach. Several research endeavors have treated consumption analysis as a knowledge discovery problem using intelligence techniques. Research Methodology

This study has two main phases i.e., design the experimental study by three variables (temperature, pressure and LHSV) for hydro-treating SOROOSH heavy oil and economical evaluation of upgrading 50,000 BPSDSOROOSH heavy oil by ARAMIS software.

3.5.1 Sources of Data and Data Collection

The approach to develop optimum parameters for upgrading Iranian heavy oil model is based on the hypothesis that first the technology used in the process should be mature and have commercial experiments for 5-8 years and preferably with high technology development. Secondly, it should be reasonable and realistic, and third it should be compatible with current situation of refineries in Iran.

Data and information necessary for this study were collected from four sources:

1- Interviews :

   a. Ministry of Petroleum. NIOC, IOOC.
   b. Limited data published by NIOC, IOOC and other International sources.
   c. Published and unpublished data from the Plan and Budget Organization of Iran.
   d. Evidence provided by earlier studies in the literature.
   e. The personal experience of researcher.

2- Site view of three most important refineries in Iran, as the main customers of upgraded oils

3- Literature review of all available and commercialized upgrading technologies

4- Lab scale analysis

i. The following steps were undertaken in this study:

   - Definition the technologies and conceptual design of facilities for upgrading heavy oils in Iran.

- Design data base based on detail process models for different variables, temperature, and pressure and space hourly liquid velocity.
- Size and cost equipment, using literature references and experimental data
- Determine total plant cost and capital investments.
- Cash flow analysis on production cost, IRR, NPV evaluation.
- Perform sensitivity analysis on major process parameters

The studies undertaken are best illustrated for chapters 4 and 5 in figures3.6 and 3.7 respectively and for overall methodology in figure 3.8.

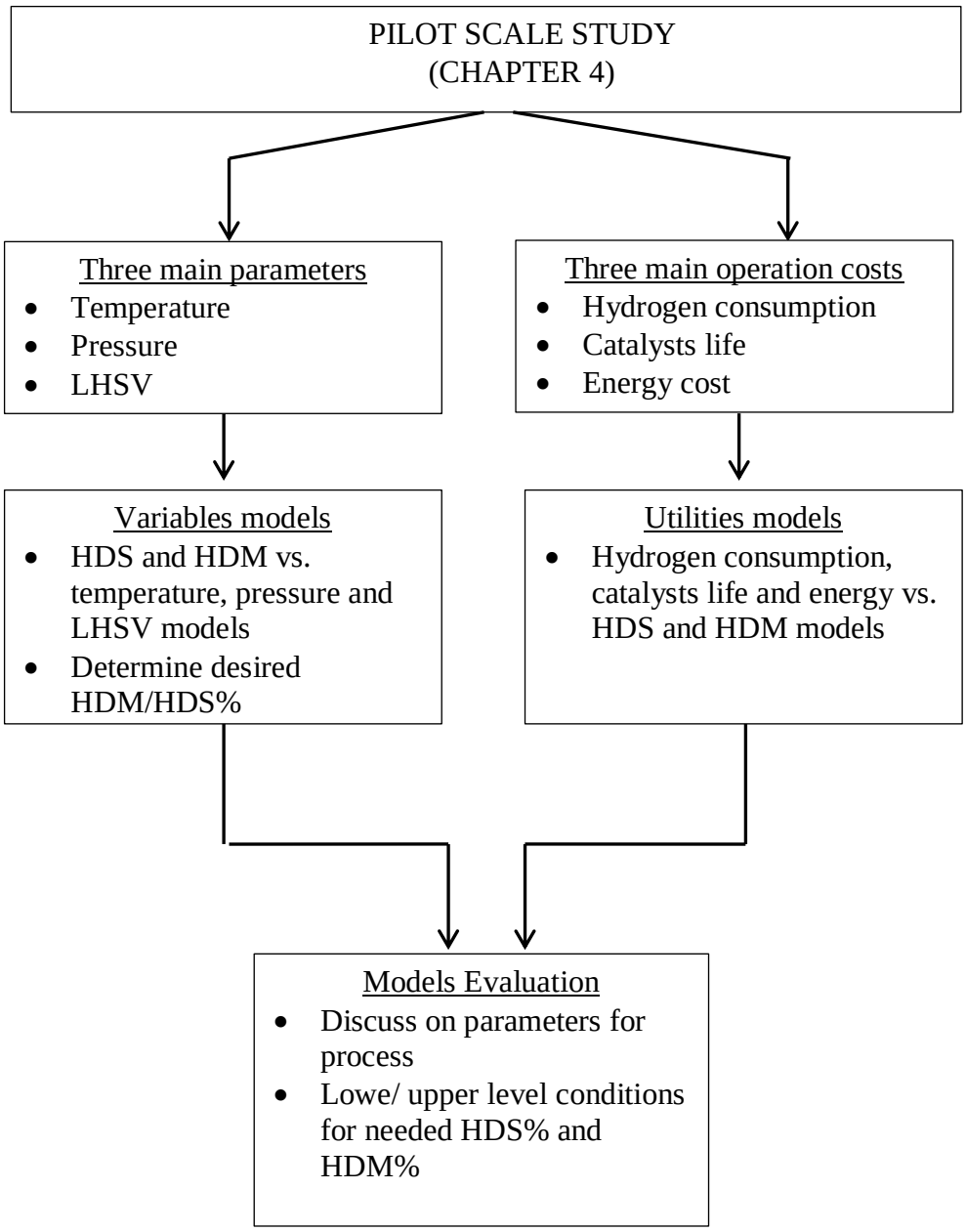

Figure 3.6: Flowchart of the research methodology of Chapter 4

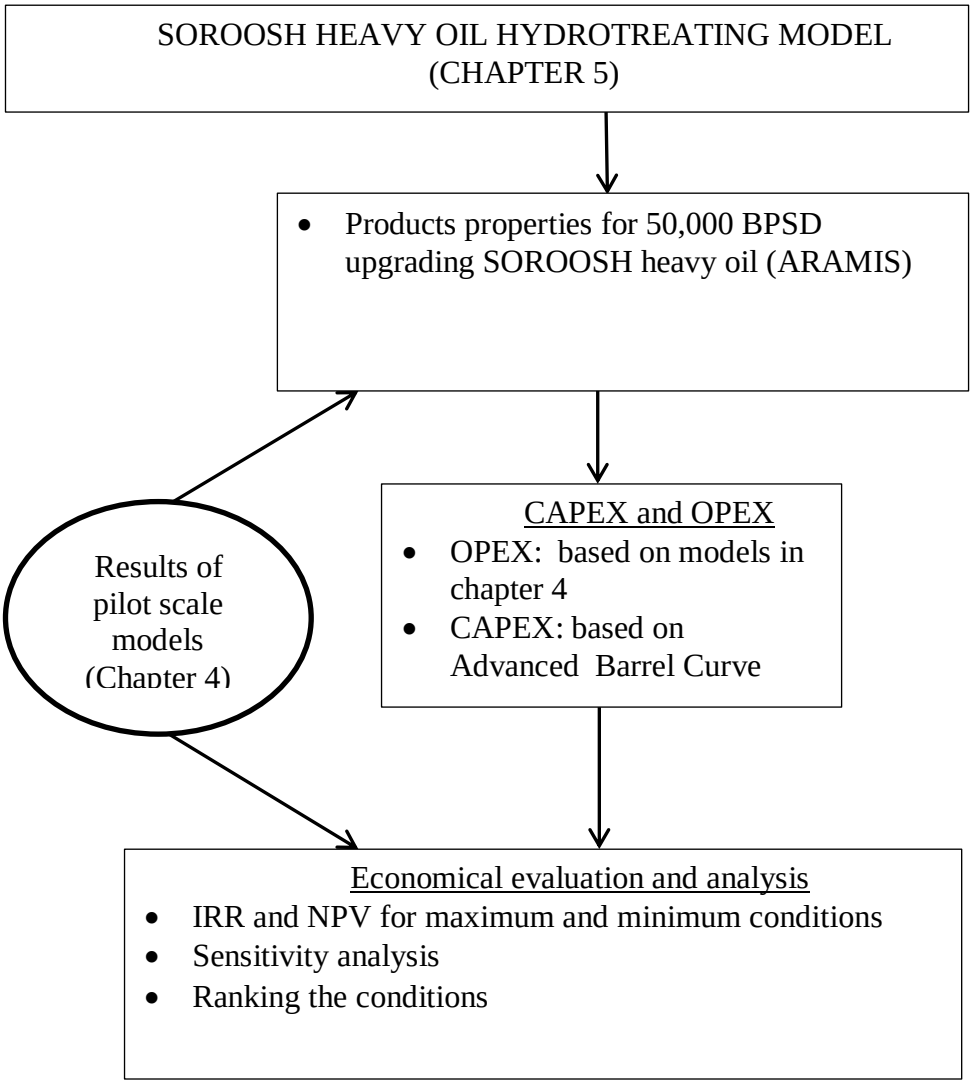

Figure 3.7:Flowchart of research methodology of Chapter 5

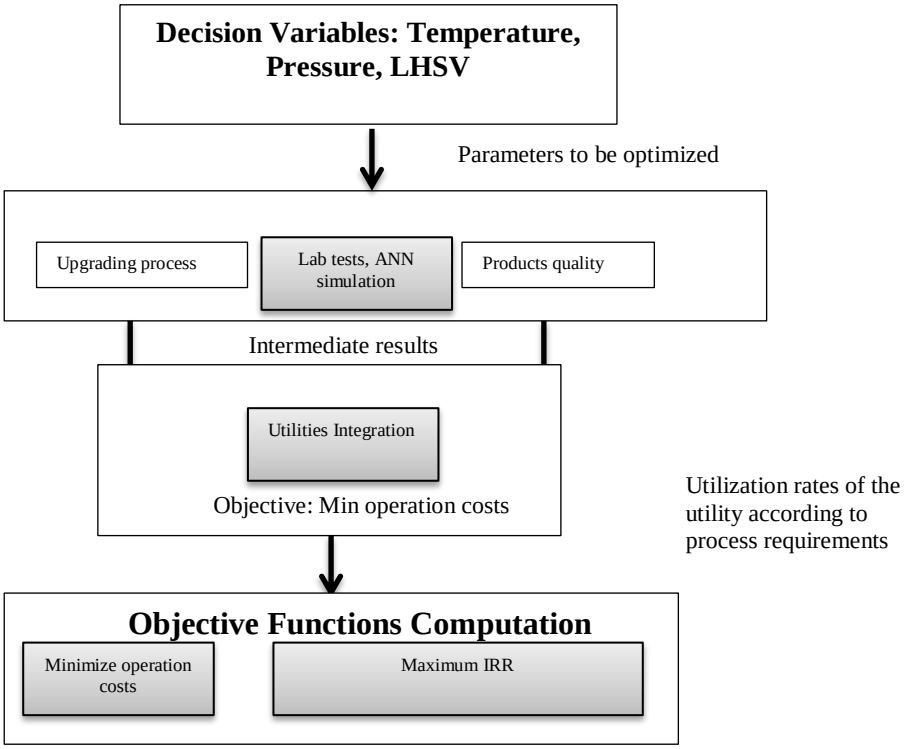

Figure 3.8: Overall Thesis Methodology (Akhavan et al., 2013)

3.6 Objective Function in This Study

The main objective of this study is to find the best condition for upgrading SOROOSH heavy oil. So the net profit function of process should be maximized. The net profit of the SOROOSH plant as a function of Operation Expenditure (OPEX),Capital Expenditure (CAPEX)and value of products as main objective and the Sub objective which includestwo functions, minimize the three main cost factors, and maximize the conversionin upgrading heavy oil are presented in equation 3.7.

Main objective: Net profit = Equation 3.7

$$\{[products\ price - (OPEX + CAPEX)\ ]\}$$

Sub objective:

$$\boldsymbol{Z = Min}\{[\boldsymbol{C_{cat} \times catalyst\ life + C_{Energy} + C_{H2} \times Total\ H2}\ )]\}$$

$$\cup$$

$$\boldsymbol{Y = Max}\{[\%\boldsymbol{HDS} \cap \%\ \boldsymbol{HDM}]\}$$

Subject to:

$60\% \leq HDS\%$

$30\% \leq HDM\%$

Where

OPEX = Operation Expenditure

CAPEX =Capital Expenditure

C_{cat}=the catalyst cost during the upgrading process that is related to the catalyst life.

$C_{Energy} = C_{Heat} + C_{Electricity} + C_{fuel}$

C_{Heat}=the cost of increasing the 1ºC heat unit of the $1m^3$feedstock to achieve the desire HDS%/HDM%

$C_{Electricity}$= Cost of all electricity consumption during the process

C_{fuel}= Cost of all fuel consumption during the

Total $H_{2=}$ is the total H_2 consumption for certain test condition

3.7 Summary

In this Chapter, the research methodology has been described and summarized in figures 3.6 and 3.7 for Chapters 4 and 5 respectively in figure 3.8 for overall methodology.

The research objective is illustrated and to achieve this objective the experimental study based on pilot plant is applied. The results associated with the various conditions are presented in Chapter 4.

CHAPTER 4: EXPERIMENTAL STUDY

4.1 Introduction

The experimental study was conducted under steady-state operation in the fixed bed high pressure pilot catalyst system. The experiments were carried out in the Research Institute of Petroleum Industry (RIPI) and licensed by Beicip-Franlab and Amirkabir University of Technology (AUT). A schematic flow diagram of the experimental unit is shown in Figure 4.1. The isothermal reactor was designed in the form of a tube with an inside diameter of 16mm and a total length of 2160 mm. It was designed to tolerate temperatures and pressures of up to 500°C and 30 MPa, respectively.

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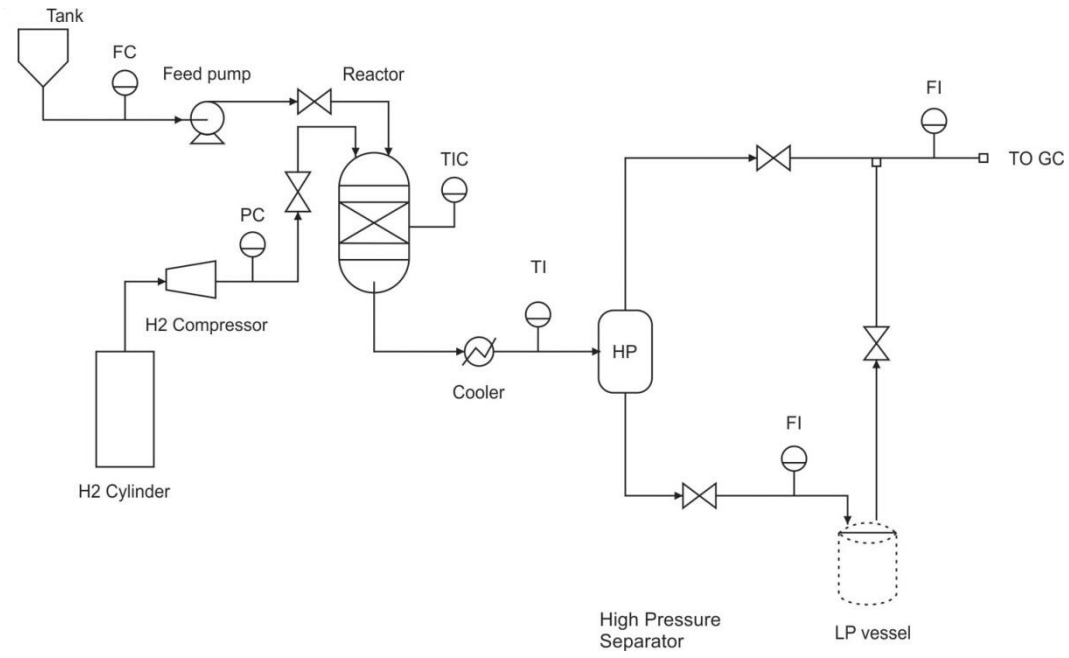

Figure 4.1: Simplified Process Flow Diagram of Hydro-Treating Set up.

FC, flow controller; PC pressure controller; TIC, temperature indicator and controller; TI, temperature indicator; HP, high pressure separator; LP, low pressure sampling vessel; FI, flow indicator; GC, gas chromatograph.

4.2 Feed Characterization

The SOROOSH crude oil properties are as shown in table 4.1 (all properties measured using standard ASTM method of analysis).

Table 4.1: SOROOSH crude oil detailed assay all cuts overview

TEST	UNIT	METHOD	WHOLE CRUDE	LIGHT ENDS	15-85C	85-150C	150-250C	250-370C	370-550C	550+
Distillation of crude oil(15plate)										
Yleid	%wt	ASTM D 2892		0.45	3.85	5.40	9.86	15.04	25.10	40.30
Yleid	%vol	ASTMD 5238		0.78	5.43	6.85	11.56	16.31	24.36	34.71
Cum.Ylied	%wt	ASTMD 2892&5238		0.45	4.30	9.70	19.56	34.60	59.70	100.00
Cum.Ylied	%vol	ASTMD 2892&5238		0.78	6.21	13.06	24.62	40.93	65.29	100.00
Density@15 °C	kg/l	ASTMD 5002/IP365/IP190	0.9356	0.5416	0.663	0.7372	0.7982	0.8627	0.9638	1.0860
Specific Gravity @60/60 ° F		CONVERSION	0.9365	0.5422	0.6636	0.738	0.799	0.8636	0.9648	1.0875
API Gravity@60 °F		CALCULATED	19.59							
Density@15 °C (dry)	kg/l	CALCULATED	0.9355							
Specific Gravity @60/60° F(dry)		CONVERSION	0.9364							
API Gravity@60 °F (dry)		CALCULATED	19.61							
Water Content	%vol	ASTMD 4298	0.1							
Light Ends										
methane	%mass	GC								
ethane	%mass	GC		6.0						
propane	%mass	GC		33.9						
i-butane	%mass	GC		11.7						
n-butane	%mass	GC		36.8						
TotalC1-C4	%mass	GC		88.4						
i-pentane	%mass	GC		4.7						
n-pentane	%mass	GC		1.7						
Heavier	%mass	GC		5.2						
Sulphur Content	%mass	ASTMD 4294	4.1	<0.01	<0.01	<0.01	0.26	1.80	3.88	6.50
(Mercaptane Sulphur)	mg/kg	ASTM D 3227			8.3	7.5	25.0	19.0	23.4	
Mercaptane Sulphur	mg/kg	UOP163	<1.0							
Total Nitrogen	%mass	ASTMD4629	0.11						0.084	0.21
(Resarch Octane Number)		ASTMD 2699				42.4				
(Pona analysis)	%vol	ASTMD 1319								
(Total paraffins)	%vol	ASTMD 1319								
(Total olefins)	%vol	ASTMD 1319			0.3	0.3	0.3			
(Total aromatics)	%vol	ASTMD 1319			2.6	10.3	22.0			
Saturates(paraffin+naphtene)	%vol	ASTMD 1319			97.1	89.4	77.7			
(Poly-N)										
(Anline Point)	°C	IP2					58	64		
(Mixed Anline Point)	°C	IP2							61	
Smoke Point	mm	IP57					28			
Naphthalene content	%vol	ASTM D 1840								
Vanadium(V)	%mass	UOP 800	122							303
Nickel (NI)	%mass	UOP 800	21							52
Irone(FE)	%mass	UOP 800	3.7							
Nickel /Vanadium Ratio			0.172							0.172
Freeze point	°C	ASTMD 2356					-51.39	-4.99		
Cloud point	°C	ASTMD 2500						-10	+27	>+50
Pour point	°C	ASTMD 5853/D97	<-38					-11	+33	>+50
Kinematic Viscosity @20 °C	mm2/s	ASTMD 445	386.8							
Kinematic Viscosity @40 °C	mm2/s	ASTMD 445	111.8					3.119		
Kinematic Viscosity @50 °C	mm2/s	ASTMD 445						4.100	84.40	
Kinematic Viscosity @80 °C	mm2/s	ASTMD 445							22.25	
Kinematic Viscosity @100 °C	mm2/s	ASTMD 445							12.70	
Kinematic Viscosity @135 °C	mm2/s	ASTMD 445								11313
Kinematic Viscosity @150 °C	mm2/s	ASTMD 445								3790
Distillation	°C	ASTMD 56								
Cetane index		ASTMD 976						49.58		
Refractive index@20 °C		ASTMD 1218						1.4796		
Refractive index@70 °C		ASTMD 1218								
Micro carbon residue	%mass	ASTMD 4530	14.6						0.50	30.3
Asphaltene	%mass	IP143	6.8							17.0
Total Acid Number	mgKOH/g	ASTM D 664	1.1							
Benzene content	%mass	GLC								
Salt content	ptb	ASTM D 3230	31							
Salt content as NACL	mg/l	IP265								
Salt content	mg/kg	IP265								
Flash point	°C	ASTMD 93(MOD)	<-5							
Sediment by Extraction	%mass	ASTM D 473	TRACE<0.05							
Reid Vapour Pressure @100 °F	psi	ASTM D 323	5.50							
Hydrogen sulphide	mg/kg	UOP163	<1.0							
Mercury	mg/kg	COLD VAPOR								
Lead	mg/kg	ASTM D 5863/AAS	<1							
Wax content	%mass	UOP46	4.21							

4.3 Pilot Scale Catalysts

The characteristics of HDT catalyst is presented in Table 4.2. Before charging the feed, the catalyst was heated up to 1300°C and then maintained at this temperature for about 6 h for drying. Then, it was sulphide with an appropriate agent according to the procedure reported by the catalyst manufacturer/supplier.(Jabbari et al., 2013)

Table 4.2: Catalyst specifications of hydro-treating process

Property	HDT
Size & Shape	1/16" &Quadralobe
Color	Green
Bulk density [kg/m^3]	750
BET Surface Area [m^2/g]	186.56
Langmuir Surface Area [m^2/g]	259.20
Average Pore Diam. (A^0)	89.09
Main Ingredients	Mo, Ni, Ti

4.4 Test Conditions

The pilot scale experiments were carried out under the following process conditions:

(1)H_2/Oil ratios = 890 m^3/m^3;

(2) LHSV=0.5, 1, 1.5h^{-1};

(3) Temperature=380°C, 400°C, 420°C

(4) Pressure =5.3, 6.9, and 9.8MPa.

The temperature of the reactor was maintained at the desired level by using a three-zone electric furnace, which provided an isothermal temperature along the active reactor section.

Note: all analytical techniques that have been used for the specifications of the feedstock and the products were accurate, fast and repeatable. Product analysis has been repeated twice for each run under each individual operating condition to ensure the accuracy of the results. All of the analyses are implemented in the laboratories of RIPI.

The hydro-treating was conducted in once-through hydrogen in down-flow. The hydrogen was of 99.8% purity. Product samples were collected at 4-8 h intervals after allowing a 2h stabilization period under each set of conditions.

4.5 Experimental Studies

Table 4.3 and 4.4 show the sulphur/metals of hydro-treating products in different LHSV, temperature and pressure, conventionally calculated on the basis of crude oil.

Table 4.3: Sulphur& Metals conversion

Tempresure (^{o}C)	Pressure (Mpa)	LHSV(h^{-1})	Sulphur (wt%)	Metal (Ni+V) (wppm)
380	9.8	0.5	1.85	90
400	9.8	0.5	1.44	77.1
420	9.8	0.5	0.83	61.2
380	9.8	1	2.2	118.00
400	9.8	1	1.85	95.41
420	9.8	1	1.22	70.1
380	9.8	1.5	2.4	122.1
400	9.8	1.5	2.18	100.70
420	9.8	1.5	1.65	88.31

Table 4.4:Sulphur& Metals conversion in different Pressure

Tempresure (^{o}C)	Pressure (Mpa)	LHSV(h^{-1})	Sulphur (wt%)	Metal (Ni+V) (wppm)
380	6.9	0.5	2.53	106.675
400	6.9	0.5	2.06	94.6
420	6.9	0.5	1.46	77.90
380	5.3	0.5	2.65	107.95
400	5.3	0.5	2.21	95.823
420	5.3	0.5	1.68	82.71

4.5.1 ANN (Artificial Neural Network) Studies:

The procedure to accomplish an ANN model for the hydro-treatment of the SOROOSH crude oil, consisted of three main steps in our study. The first step was to construct a knowledge database from samples used for the ANN model. The second step was to select an ANN structure and determine its parameters. Finally, the third step was to carry out a regression (training) on the ANN model.

To determine the number of layers and the neurons, some authors suggested using the heuristic rules (Beale et al., 2011) or to apply systematic methodologies such as pruning and growing, and take approaches based on genetic algorithms. However, for simplicity, the number of layers and neurons were chosen by the trial and error method (Heaton, 2005).

In this study ANN was used to model the sulphur and metals conversion in the upgrading process. The structure of neural network was defined as 3:10:1 multilayer perceptron neural network with the use of back-propagation training algorithm. The MLP type of network with 4 neurons in the hidden layer proved to be optimal considering the ANN's complexity and accuracy as shown in Figure 4.2, where temperature, pressure and LHSV are the input control variables (x_i) and sulphur and metal conversion are the output (u_k). The summary of input and output variables for the neural network model were collected from the hydro-treating experimental process and are shown in tables 4.5 and 4.6.

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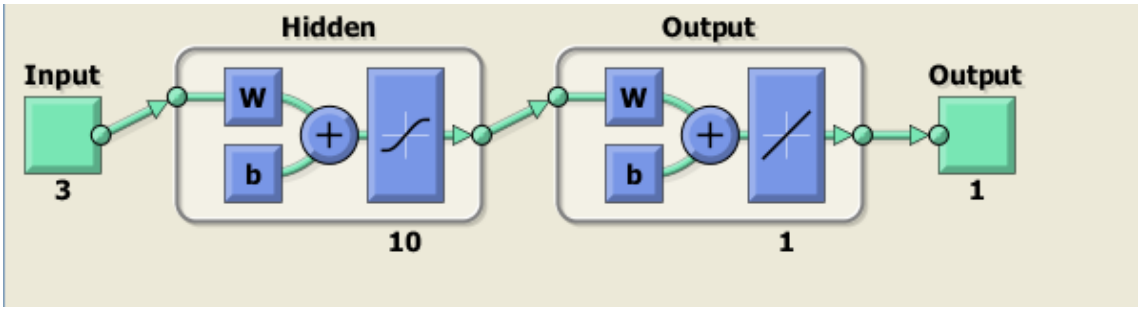

Figure 4.2: Structure of a three-layer artificial neural network

Table 4.5: Summary of input variables

Factors	Symbol	Unit
Temperature	T	°C
Pressure	P	MPa
Liquid Hourly Space Velocity	LHSV	h^{-1}
Sulphur	S	%wt.
Heavy metals	Metals	wppm

Table 4.6: Input–output data for ANN in upgrading process

x_1 (°C)	x_2 (MPa)	x_3 (h^{-1})
380	9.8	0.5
400	9.8	0.5
420	9.8	0.5
380	9.8	1
400	9.8	1
420	9.8	1
380	9.8	1.5
400	9.8	1.5
420	9.8	1.5
380	6.9	0.5
400	6.9	0.5
420	6.9	0.5
380	5.3	0.5
400	5.3	0.5
420	5.3	0.5

The corresponding plots which are indicated the simulation results for sulphur and metals conversion vs. temperature and pressure in different LHSV shown in figure 4.3 and 4.4 respectively.

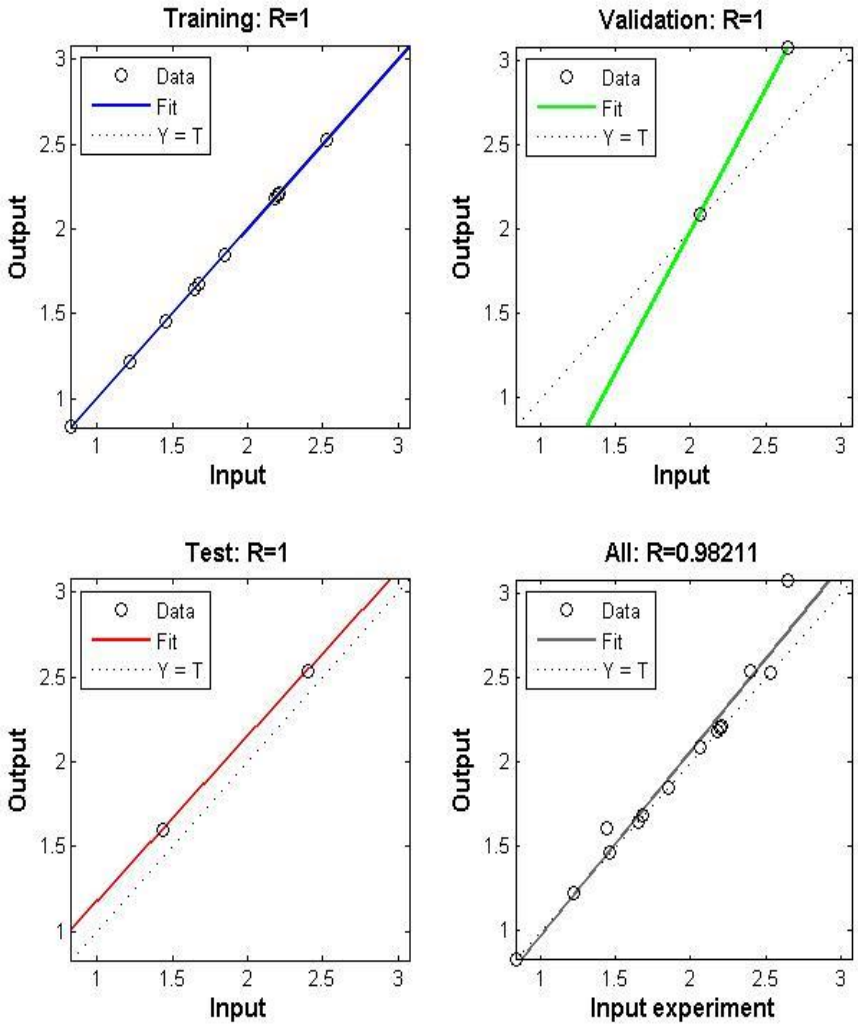

Figure 4.3: Sulphur conversion prediction by ANN

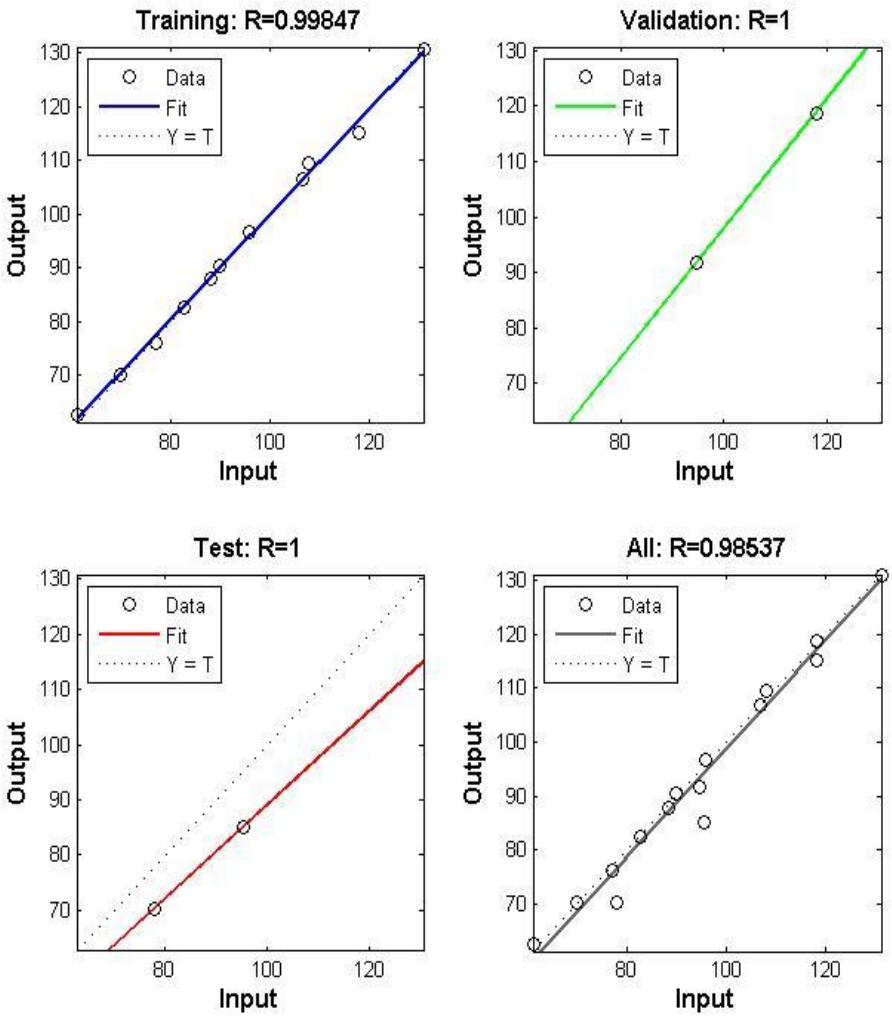

Figure 4.4: Metals conversion prediction by ANN

Table 4.7 reports the performance of ANN in terms of Mean Absolute Error (MAE) and the R between experimental data and neural network outputs. As in Table 4.7, MSE of ANN model is considerably small and R is close to 1. These indicate that training performance of ANN model is good. The number of iterations for sulphur and metals are 6 and 8 respectively.

Table 4.7: ANN performance for Sulphur and Metals

Performance	Sulphur	Metals
MAE	0.08	2.23
R	0.982	0.985

Table 4.8: The forecastin g results of the model for Sulphur

Tempresure (C^0)	**Pressure (Mpa)**	**LHSV(h^{-1})**	**Actual outputs (wt%)**	**Model outputs(wt%)**	**Relative error (%)**
380	6.9	1	2.73	2.63	3.85
400	6.9	1	2.37	2.30	3.14
420	6.9	1	1.85	1.82	1.63
380	6.9	1.5	2.85	2.74	4.15
400	6.9	1.5	2.59	2.45	5.73
420	6.9	1.5	2.19	2.10	4.50
380	5.3	1	2.83	2.92	3.08
400	5.3	1	2.47	2.40	2.96
420	5.3	1	2.01	2.09	3.68
380	5.3	1.5	2.97	2.96	0.21
400	5.3	1.5	2.74	2.66	3.05
420	5.3	1.5	2.4	2.35	2.27

Table 4.9: **The forecastin g results of the model for Metals**

Tempresure (C^0)	Pressure (Mpa)	LHSV(h^{-1})	Actual outputs (wt%)	Model outputs(wt%)	Relative error (%)
380	6.9	1	131.2	133.24	1.53
400	6.9	1	113	113.38	0.34
420	6.9	1	86.2	80.37	-7.26
380	6.9	1.5	141.4	140.74	-0.47
400	6.9	1.5	119.91	121.79	1.54
420	6.9	1.5	100	95.65	-4.55
380	5.3	1	133.7	133.77	0.05
400	5.3	1	117.3	116.57	-0.63
420	5.3	1	93.7	86.81	-7.94
380	5.3	1.5	141.70	141.80	0.07
400	5.3	1.5	127.1	128.42	1.02
420	5.3	1.5	105.1	102.65	-2.39

The results of prediction of ANN are presented in table 4.8 and 4.9. In Table 4.8 and 4.9, the forecasting results of ANN are compared to the experimental data for sulphur and metals respectively. As in these tables, the average relative error of forecasting results of the ANN models are 3.18% and 2.15% for sulphur and metals respectively. It can be proved that the models have good ability of forecasting conversion process.

The ability of ANN in developing models for very complicated plant and analyzing the plant was confirmed. Based on current increasing experimental study costs, the developed model easily can give us the results while this is very difficult to achieve using traditional model.

4.6 Experimental Models

The hydro-treating experiments focused on studying the effect of key process variables on the conversion of sulphur and metals for the SOROOSH crude oil. The process parameters included: reactor pressure; reaction temperature; LHSV and hydrogen-to-oil ratio (H_2/Oil) (that was kept constant throughout our experiments). These were selected to determine the effect of altering a particular variable on heteroatom's removal process. Each experiment was conducted by altering one variable at a time.

The effect of the reaction temperature on synthetic crude oil quality was studied between 380°C and 420°C, and the other variables were modified within the ranges shown in Table 4.10.

Table 4.10: Operation condition in upgrading process

Pressure (MPa)	**9.8, 6.9, 5.3**
LHSV(h^{-1})	0.5,1.0,1.5
H_2/Oil(m^3/m^3)	890

The effects of temperature and LHSV on sulphur and metals content in products are presented in figures 4.5 to 4.7 for sulphur and 4.8 to 4.10 for metals. These experiments were carried out in constant H_2/Oil ratios of 890 m^3/m^3

The Figures 4.5 to 4.10, indicate that under the conditions where the temperature is 420^{o}C, LHSV=0.5h^{-1} and the pressure is 9.8 MPa. (Severe condition) the sulphur/metals content in the products is at its lowest level.

The level of sulphur/metals content in the products started decreasing at an operating temperature of 380^o C and this decrease further accelerated when the pressure increased and the temperature raised to 400^{o}C or 420^{o}C.

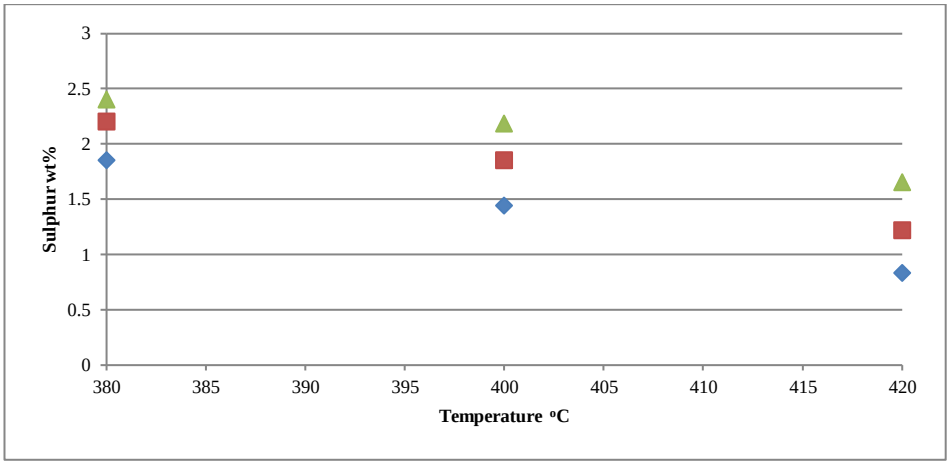

Figure 4.5: Sulphur (%wt.) vs. Temperature. (H_2/Oil ratios = 890 m^3/m^3, P=9.8MPa
(♦) LHSV=0.5h^{-1}, (■) LHSV=1.0h^{-1}, (▲) LHSV=1.5h^{-1}

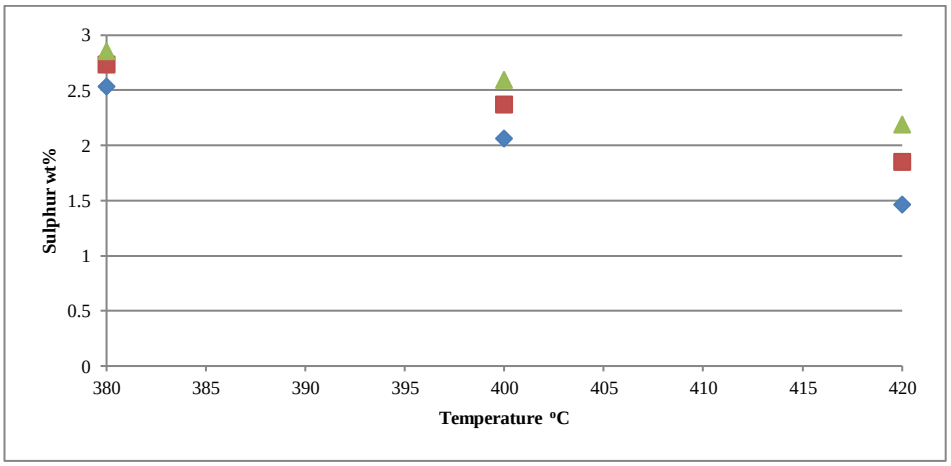

Figure 4.6: Sulphur (%wt.) vs. Temperature. (H_2/Oil ratios = 890 m^3/m^3, P=6.9MPa
(♦) LHSV=0.5h^{-1}, (■) LHSV=1.0h^{-1}, (▲) LHSV=1.5h^{-1}

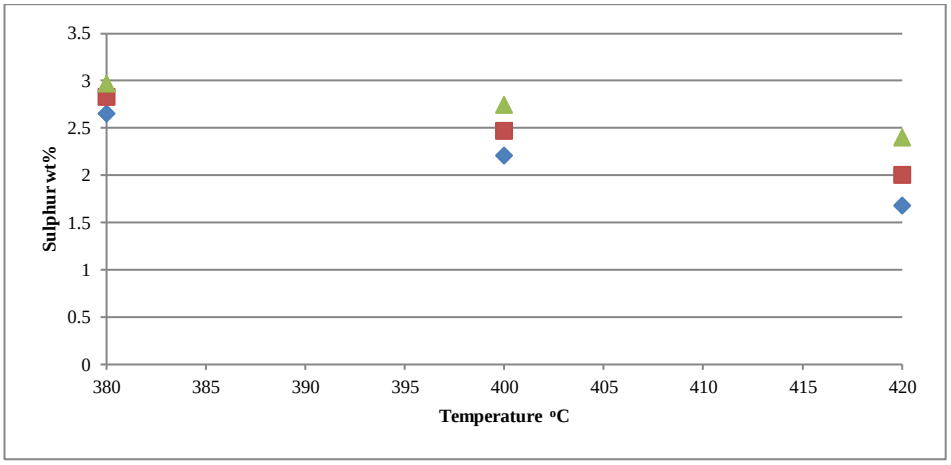

Figure 4.7: Sulphur (%wt.) vs. Temperature. (H_2/Oil ratios = 890 m^3/m^3, P=5.3MPa
(♦) LHSV=0.5h^{-1}, (■) LHSV=1.0h^{-1}, (▲) LHSV=1.5h^{-1}

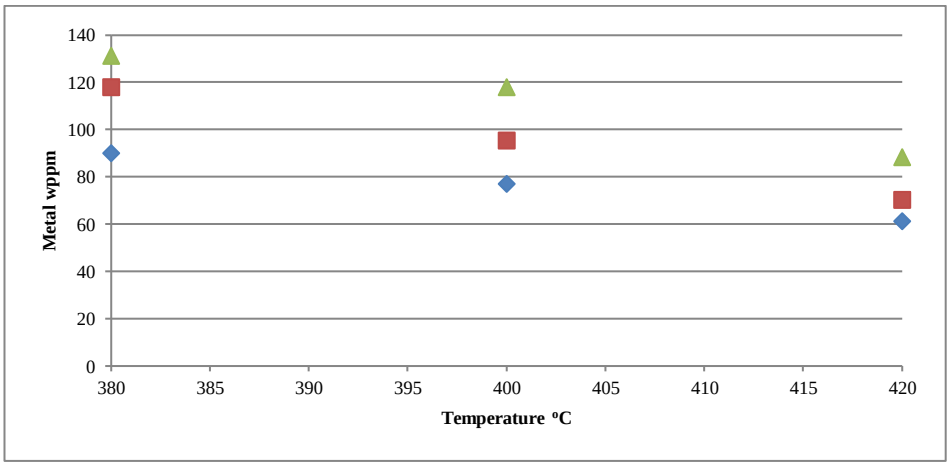

Figure 4.8: Metals (wppm) vs. Temperature.(H_2/Oil ratios = 890 m^3/m^3, P=9.8MPa
(♦) LHSV=0.5h^{-1}, (■) LHSV=1.0h^{-1}, (▲) LHSV=1.5h^{-1}

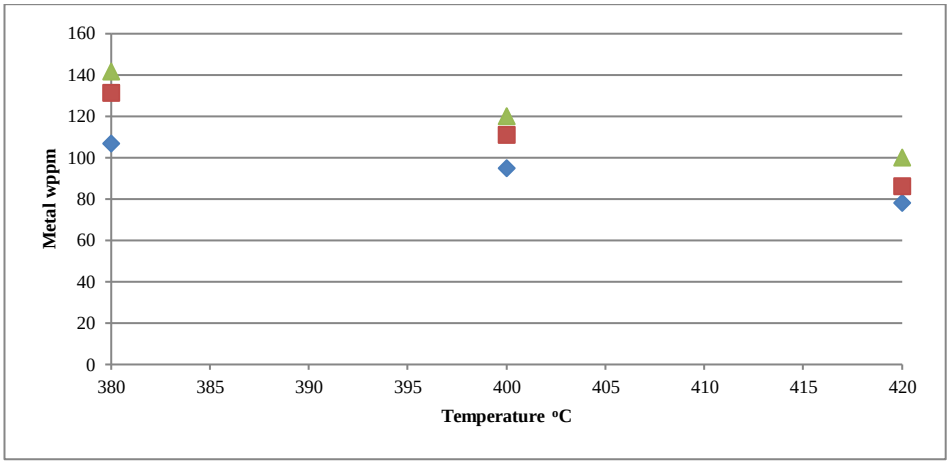

Figure 4.9: Metals (wppm) vs. Temperature. (H_2/Oil ratios = 890 m^3/m^3, P=6.9MPa
(♦) LHSV=0.5h^{-1}, (■) LHSV=1.0h^{-1}, (▲) LHSV=1.5h^{-1}

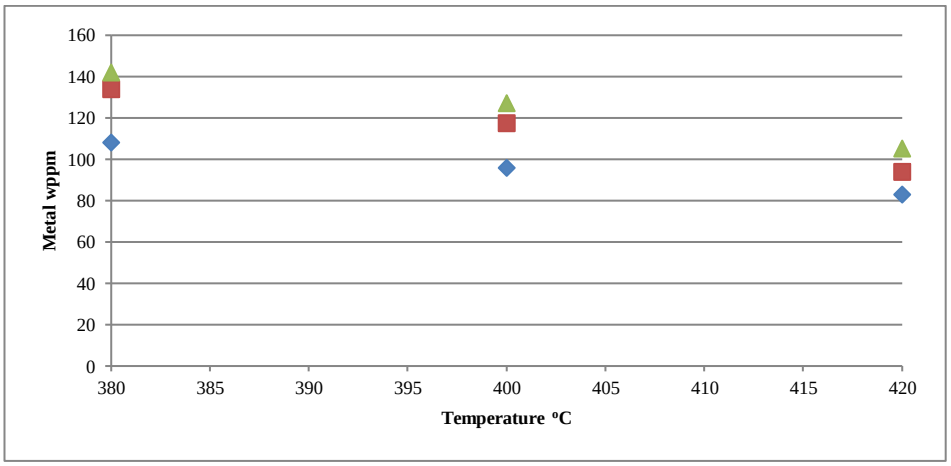

Figure 4.10: Metals (wppm) vs. Temperature. (H_2/Oil ratios = 890 m^3/m^3, P=5.3MPa
(♦) LHSV=0.5h^{-1}, (■) LHSV=1.0h^{-1}, (▲) LHSV=1.5h^{-1}

The pressure effects on the hydro-treating for SOROOSH crude oil are given in figure 4.11 to 4.13 for sulphur and 4.14 to 4.16 for metals.

Different reactor pressures within the range of 5.3 to 9.8 MPa were set and meanwhile for each step of the reactor pressure the results were collected under 380°C, 400°C, and 420°C reaction temperature for each of the LHSV steps of 0.5, 1.0, 1.5 h^{-1}

These figures show that at higher reactor pressure the product quality improved significantly. The sulphur and metals contents were considerably reduced when the pressure was changed from 6.9 to 9.8 MPa. The HDS and HDM levels were at 78% and 57% respectively under the highest pressure and temperature values (i.e. 9.8 MPa & 420°C)

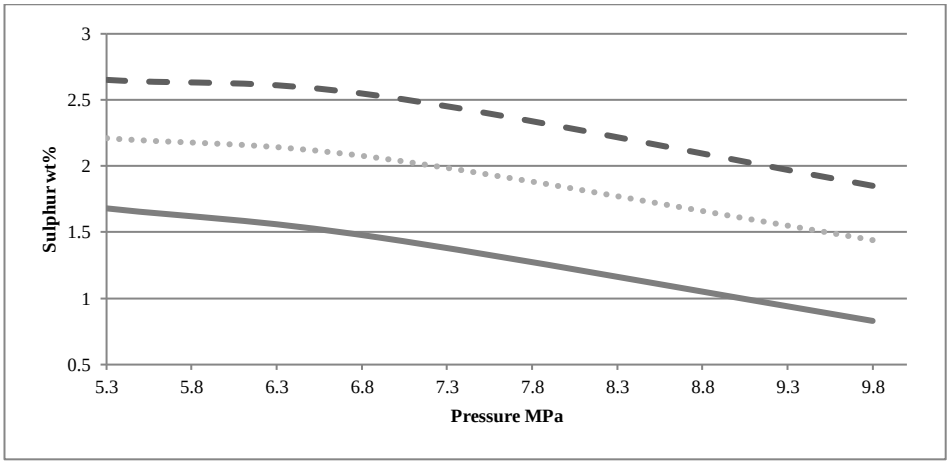

Figure 4.11: Sulphur (%wt.) vs. Pressure. (H_2/Oil ratios=890 m^3/m^3, LHSV=0.5h^{-1}
(---) T=380°C, (….) T=400°C, (___) T=420°C)

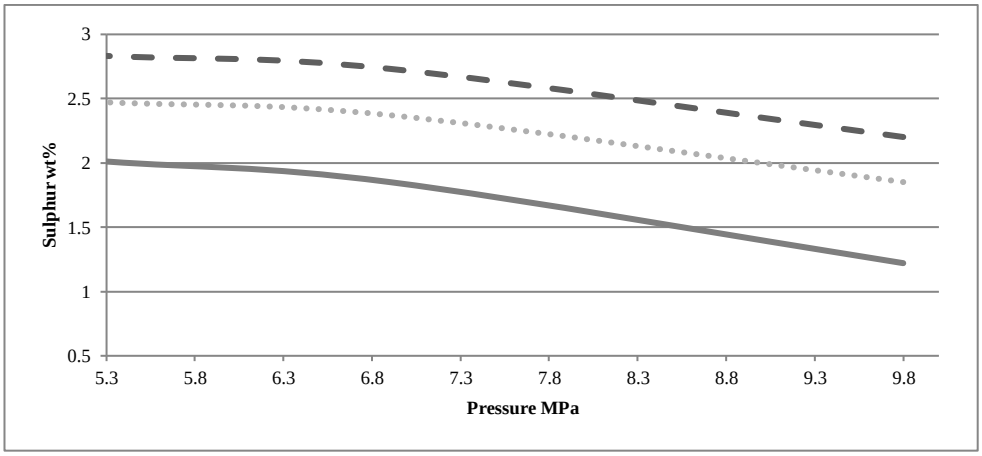

Figure 4.12:Sulphur(%wt.) vs.Pressure. (H_2/Oil ratios=890 m^3/m^3, LHSV=1.0h^{-1}
(---) T=380°C, (….) T=400°C, (___) T=420°C)

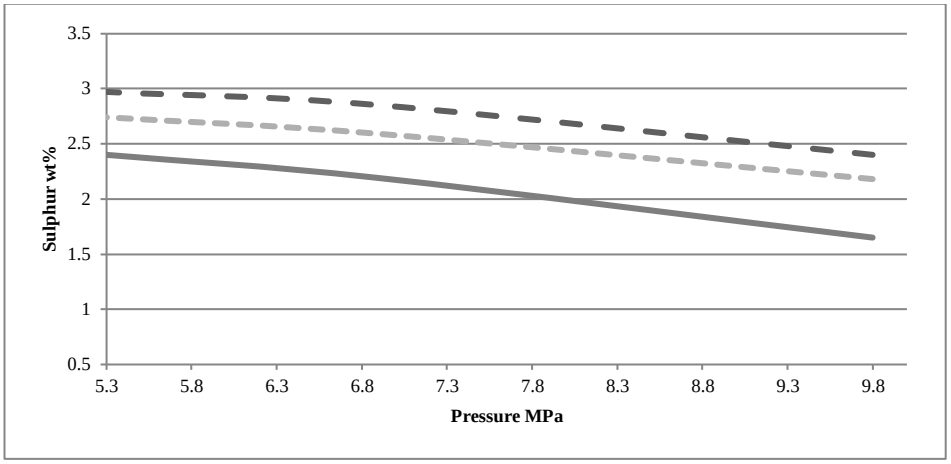

Figure 4.13:Sulphur (%wt.) vs. Pressure. (H_2/Oil ratio=890 m^3/m^3, LHSV=1.5h^{-1} (---) T=380°C, (….) T=400°C, (___) T=420°C)

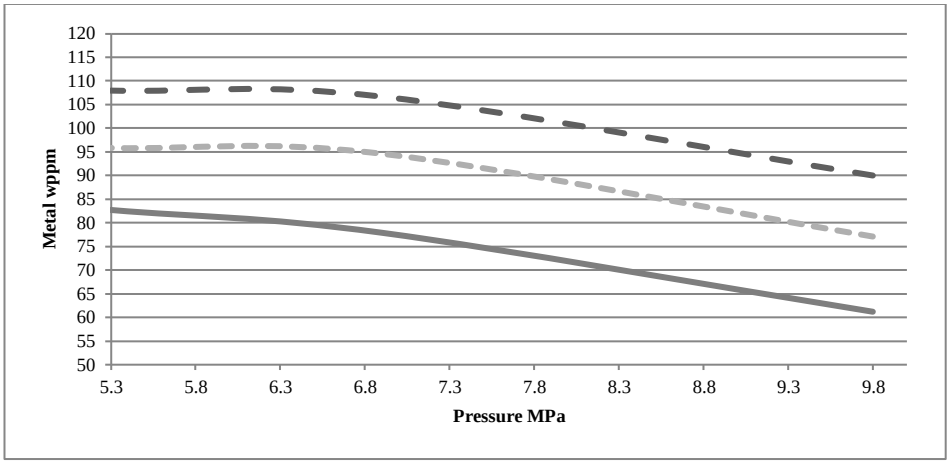

Figure 4.14:Metals(wppm) vs. Pressure.(H_2/Oil ratios=890 m^3/m^3, LHSV=0.5h^{-1} (---) T=380°C, (….) T=400°C, (___) T=420°C)

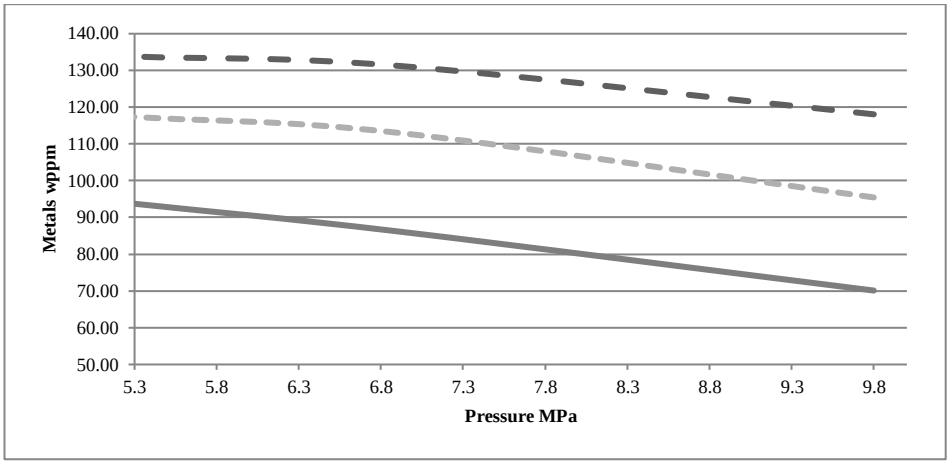

Figure 4.15:Metals(wppm) vs. Pressure. (H_2/Oil ratios=890 m^3/m^3,LHSV=1.0h^{-1} (---) T=380^{o}C, (….) T=400^{o}C, (___) T=420^{o}C)

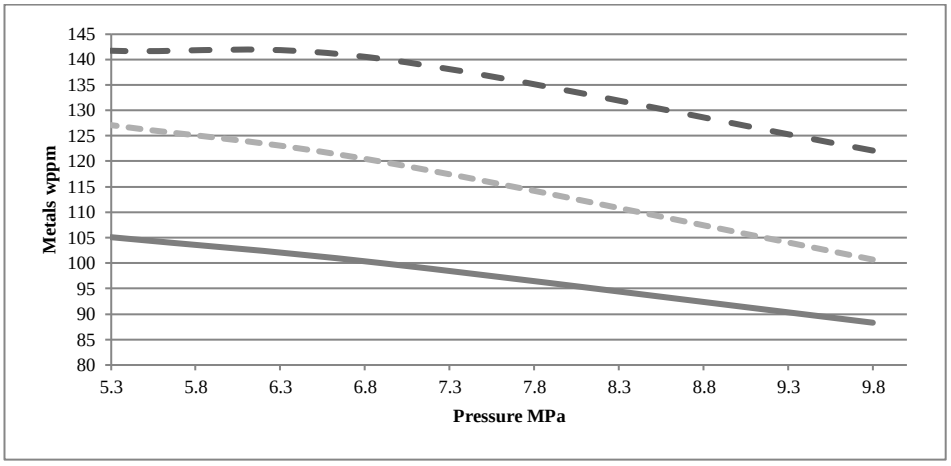

Figure 4.16:Metals(wppm) vs. Pressure. (H_2/Oil ratios=890 m^3/m^3, LHSV=1.5h^{-1} (---) T=380^{o}C, (….) T=400^{o}C, (___) T=420^{o}C)

4.7 Determination of Models Accuracy

The goodness of fit for developed models was checked with the analysis of variance (ANOVA) using Fischer's exact test with 95% probability (Montgomery, 2013).

In this study the statistical tests (R^2 test, adjusted R^2, Mean Squared Error (*MSE*), Sum Squared Error (*SSE*) and Root Mean Squared Error (*RMSE)*) were used to evaluate the accuracy of the developed models.

The use of "test of significance" for the factors indicates that insignificant factors or interactions should be ignored in the model. The Significance of the factors or the

interactions were evaluated using the P-value (probability value). When a P-value for a factor or an interaction is greater than 0.05, it is 95% certain that the factor or interaction is insignificant and can therefore be ignored in the final mathematical model. R^2, a value that always falls between 0 and 1, is the relative predictive power of a model. The closer to 1 the R^2 is, the better the model represents the experimental observations. However, it should be noted that by simply incorporating more factors or interactions, R^2 may be increased but the predictive power of the model may not be improved. Because of this shortcoming of R^2, the use of adjusted R^2 is advised. Adjusted R^2 is a modification of R^2, but unlike R^2, it only increases when the newly included factor(s) or interaction(s) are significant. Another quantity is predicted R^2. While R^2 indicates how well the model fits the experimental data at hand, predicted R^2 indicates how well the model predicts responses for new observations.

4.7.1 Effect of the variables on Sulphur/Metal Conversion:

The R^2, adjusted R^2, *SSE, p-value,* values of the factors and interactions of the developed correlations are summarized in Tables 4.10 to 4.12 for sulphur and 4.13 to 4.16 for metals.

In table 4.10 the values for R^2 and adjusted R^2 are; 0.958, 0.983, 0.992 and 0.917, 0.965, 0.985 respectively, indicating the accuracy of the models. The other models' accuracy are acceptable because of the values for R^2 and adjusted R^2 in tables 4.11 to 4.16.

The P-values at T=380^{o}C, T=400^{o}C and T=420^{o}C are 0.061, 0.045 and 0.032 respectively (table 4.10). It means that when the temperature is low the effect of pressure is not considerable; however by increasing the temperature the effect of pressure becomes significant. As shown in the table 4.11 when the LHSV increases, the

effect of the pressure becomes more important and when the LHSV increases to $1.5h^{-1}$ as shown in the table 4.12, the pressure becomes more significant.

When we compare the P-values in the tables 4.10 to 4.12, we can obsereve that when LHSV is $0.5h^{-1}$ in low temperature (T=380°C) the effect of the pressure on HDS is not significant and this trend changes when the temperature increases up to 420°C , but when the LHSV becomes $1.5h^{-1}$the effect of the pressure becomes momentous on all temperatures. On the other hand the role of the pressure on HDM at LHSV= $0.5h^{-1}$ and T=380°C is notable but at 400°C it diminishes and increases again when the temperature reaches to 420°C.

Therefore, the experimental studies and the relevant literatures support the idea that the tempreture and LHSV have remarkable effects on HDS% and HDM%. It means that temperature and LHSV are two major operating parameters for the hydro-treatment processes and the effect of the pressure is minor . Also, it should be noted that the type of the catalyst can be considered as an important factor. Since finding operating conditions and controlling the process, are important, evaluating the catalyst and estimating the hydrogen consumption can be important too.

This trend continues for the rest of the analysis and proves the following concepts (tables 4.13 to 4.16):

I. The reaction temperature is certainly the most influential variable in the process. The extent and selectivity of HDT reactions are very sensitive to this process condition. Therefore, temperature is considered the easiest and most cost-effective variable to control the hydro-treatment process. An increase in temperature increases both the rate and conversion of the process.

II. The coefficient rate of HDS and the reaction temperature is exponential, so the reaction temperature is generally matched to the chemistry of the process in order to achieve the desired selectivity (figure 4.5 to 4.7).

III. The functions of HDS%/HDM% vs. temperature and LHSV at different pressures help us to find the maximum and minimum conditions for maximum and minimum HDS% and HDM% respectively.

Table 4.11: **Sulphur conversion model in LHSV(0.5h^{-1}), P=(5.3, 6.9, 9.8MPa)**

	T=380°C	T=400°C	T=420°C
R Square	0.958	0.983	0.992
Adjusted R Square	0.917	0.965	0.985
SSE	0.170	0.112	0.067
P-value	0.061	0.045	0.032

Table 4.12:**Sulphur conversion model in LHSV (1.0h^{-1}), P=(5.3, 6.9, 9.8MPa)**

	T=380°C	T=400°C	T=420°C
R Square	0.947	0.974	0.973
Adjusted R Square	0.895	0.949	0.946
SSE	0.129	0.098	0.067
P-value	0.050	0.045	0.023

Table 4.13: **Sulphur conversion model in LHSV (1.5h^{-1}), P=(5.3,6.9,9.8 MPa)**

	T=380°C	T=400°C	T=420°C
R Square	-	0.998	1.000
Adjusted R Square	-	0.997	0.999
SSE	-	0.012	0.006
P-value	-	0.005	0.003

Table 4.14:**Metals conversion model in LHSV (0.5h^{-1}), P= (5.3, 6.9, 9.8MPa)**

	T=380°C	T=400°C	T=420°C
R Square	0.916	0.913	0.980
Adjusted R Square	0.831	0.825	0.959
SSE	4.173	4.136	2.283
P-value	0.054	0.046	0.031

Table 4.15:**Metals conversion model in LHSV (1.0h^{-1}), P= (5.3, 6.9, 9.8MPa)**

	T=380°C	T=400°C	T=420°C
R Square	0.957	0.971	0.998
Adjusted R Square	0.913	0.941	0.996
SSE	2.805	2.482	0.718
P-value	0.029	0.024	0.009

Table 4.16: **Metals conversion model in LHSV (1.5h^{-1}), P= (5.3, 6.9, 9.8MPa)**

	T=380°C	T=400°C	T=420°C
R Square	-	0.992	0.997
Adjusted R Square	-	0.983	0.993
SSE	-	1.769	0.700
P-value	-	0.017	0.008

The figures 4.17 to 4.19 and 4.20 to 4.22 show the sulphur and metals conversions vs. temperature and LHSV respectively and table 4.16 presents the accuracy of models.

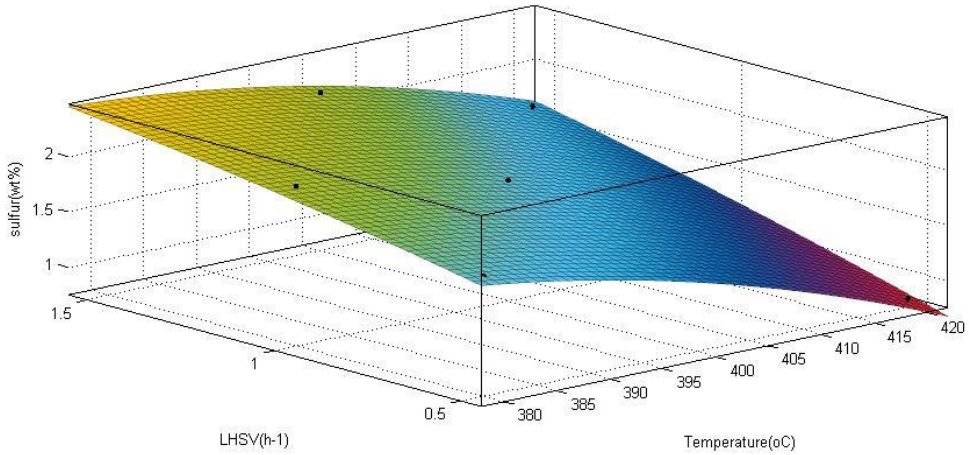

Figure 4.17:Sulphur(%wt.)vs.Temperature&LHSV, (H_2/Oil=890m^3/m^3, P=9.8 MPa)

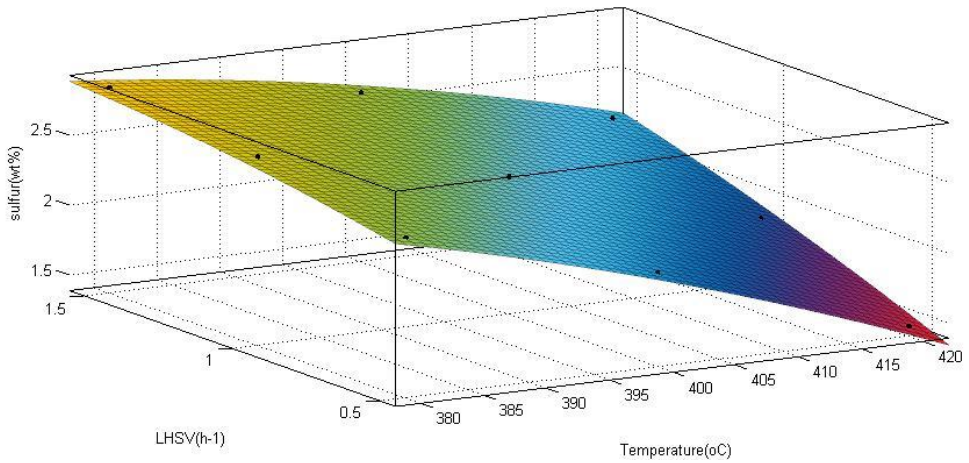

Figure 4.18:Sulphur(%wt.)vs.Temperature&LHSV, (H_2/Oil=890 m^3/m^3, P=6.9 MPa)

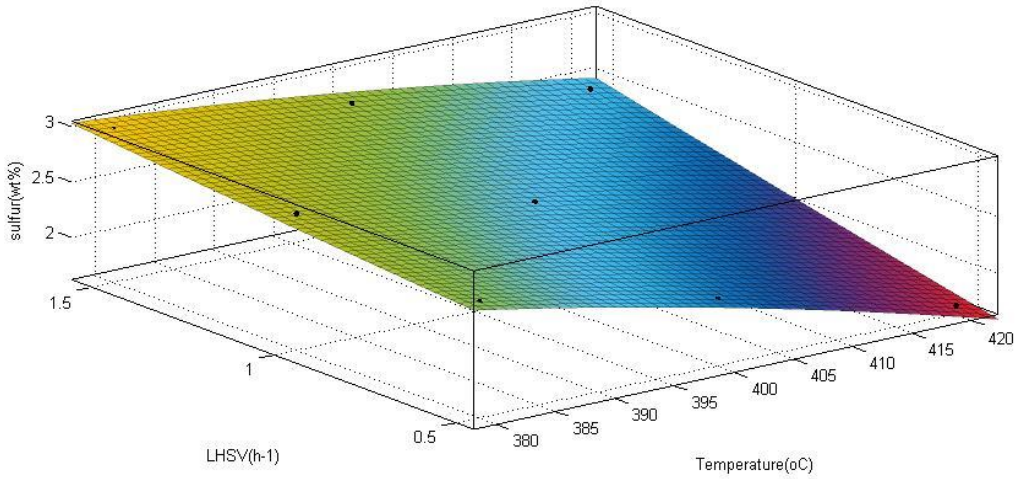

Figure 4.19:Sulphur(%wt.)vs.Temperature&LHSV, (H_2/Oil=890 m^3/m^3, P=5.3 MPa)

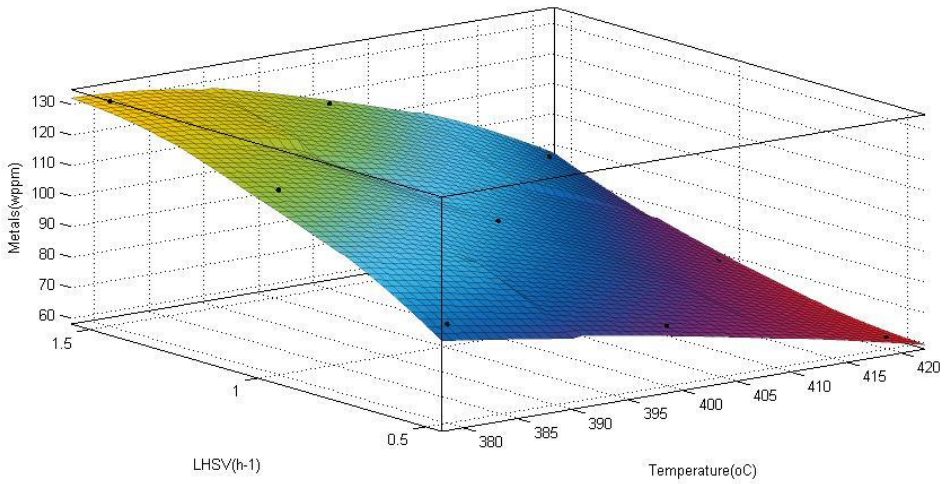

Figure 4.20:Metals(wppm)vs.Temperature&LHSV,(H_2/Oil=890 m^3/m^3, P=9.8 MPa)

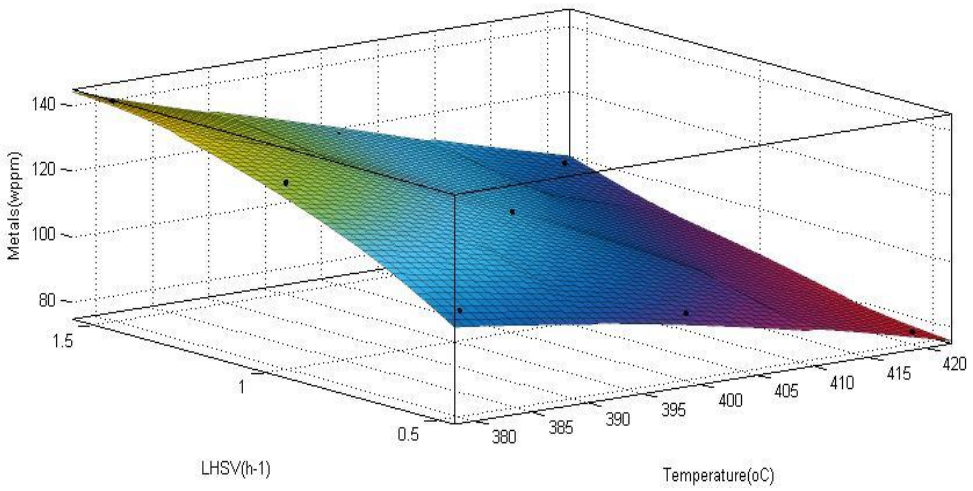

Figure 4.21:Metals(wppm)vs.Temperature&LHSV,(H_2/Oil=890 m^3/m^3, P=6.9MPa)

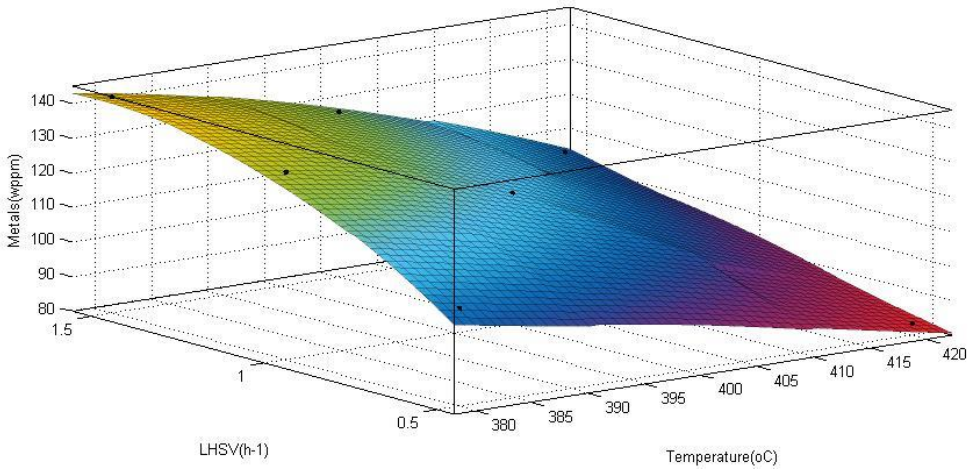

Figure 4.22:Metals(wppm)vs.Temperature&LHSV,(H_2/Oil=890 m^3/m^3, P=5.3MPa)

Table 4.17: Statistics analysis for the Models

Model	*SSE*	R^2	adjusted R^2	RMSE
Sulphur(%wt.) vs. Temperature and LHSV Pressure=9.8 MPa	0.004086	0.998	0.9947	0.03691
Sulphur (%wt.) vs. Temperature and LHSV Pressure=6.9MPa	0.0001528	0.9999	0.9997	0.007136
Sulphur (%wt.) vs. Temperature and LHSV Pressure=5.3MPa	0.001203	0.9991	0.9977	0.02002
Metals(wppm)vs. Temperature and LHSV Pressure=9.8 MPa	8.449	0.9981	0.9968	1.334
Metals(wppm)vs. Temperature and LHSV Pressure=6.9MPa	3.618	0.9989	0.9982	0.8728
Metals(wppm)vs. Temperature and LHSV Pressure=5.3MPa	3.162	0.999	0.9983	0.8158

4.8 Maximum/Minimum Desired Conditions

In this study, Genetic Algorithms (GA) can be used to solve the objective functions for a near-optimal condition for upgrading SOROOSH heavy oil. So to find the best conditions, the sulphur and metals contents in products, were estimated as functions of temperature, pressure and LHSV. (Table 4.18, Table 4.19)(Appendix B)

Table 4.18: Sulphur and Metals function's vs. temperature

Y= Sulphur, X= Temperature	**Y= Metals, X= Temperature**
Pressure 9.8, LHSV= 0.5 **$y = 3942.8e^{-0.02x}$**	Pressure 9.8, LHSV= 0.5 y = -1.6475x + 743.87
Pressure 9.8, LHSV= 1.0 **$y = 620.32e^{-0.015x}$**	Pressure 9.8, LHSV= 1.0 y = -1.5285x + 709.2
Pressure 9.8, LHSV= 1.5 **$y = 86.961e^{-0.009x}$**	Pressure 9.8, LHSV= 1.5 y = -1.2447x + 612.07
Pressure 6.9, LHSV= 0.5 **$y = 480.24e^{-0.014x}$**	Pressure 6.9, LHSV= 0.5 y = -1.359x + 639.79
Pressure 6.9, LHSV= 1.0 **$y = 112.01e^{-0.01x}$**	Pressure 6.9, LHSV= 1.0 y = -1.295x + 622.57
Pressure 6.9, LHSV= 1.5 **$y = 35.227e^{-0.007x}$**	Pressure 6.9, LHSV= 1.5 y = -1.035x + 534.44
Pressure 5.3, LHSV= 0.5 **y = -0.0242x + 11.88**	Pressure 5.3, LHSV= 0.5 y = -1.0321x + 519.86
Pressure 5.3, LHSV= 1.0 **y = -0.0207x + 10.724**	Pressure 5.3, LHSV= 1.0 y = -x + 514.9
Pressure 5.3, LHSV= 1.5 **y = -0.0143x + 8.4033**	Pressure 5.3, LHSV= 1.5 y = -0.915x + 490.63

Table 4.19: GA simulation for lower level conversion conditions

Y= Sulphur, X= Temperature	**Y= Metals, X= Temperature**
Pressure 9.8, LHSV= 0.5 **T1= 390.82** **Y1= 1.59**	Pressure 9.8, LHSV= 0.5 T1= 390.82 Y1= 100
Pressure 9.8, LHSV= 1.0 **T2= 398** **Y2= 1.58**	Pressure 9.8, LHSV= 1.0 T2= 398 Y2= 99
Pressure 9.8, LHSV= 1.5 **T3= 412** **Y3= 1.6**	Pressure 9.8, LHSV= 1.5 T3= 412 Y3= 98
Pressure 6.9, LHSV= 0.5 **T4= 407.45** **Y4= 1.6**	Pressure 6.9, LHSV= 0.5 T4= 407.45 Y4= 86.07

4.9 Summary

In this chapter, the experimental results of the upgrading of SOROOSH crude oil in a pilot plant were presented and discussed. Then, some results were predicted by ANN for HDS and HDM, and the performance was evaluated to show the accuracy of the prediction. The ANOVA analysis was done to find out the effect of the three hydro-treating parameters on HDS and HDM. The results proved that the temperature and LHSV were the two most effective parameters in the upgrading process. Based on the sub objective in section 3.6 in chapter 3, the H_2 consumption, catalyst's life and the energy consumption functions for HDS and HDM based on the experimental results were depicted. After solving the functions with regards to the sub objective; the two Upper Level (UL)(Y) and Lower Level (LL) (Z) ranges were obtained. These two ranges are shown in figure 4.33.

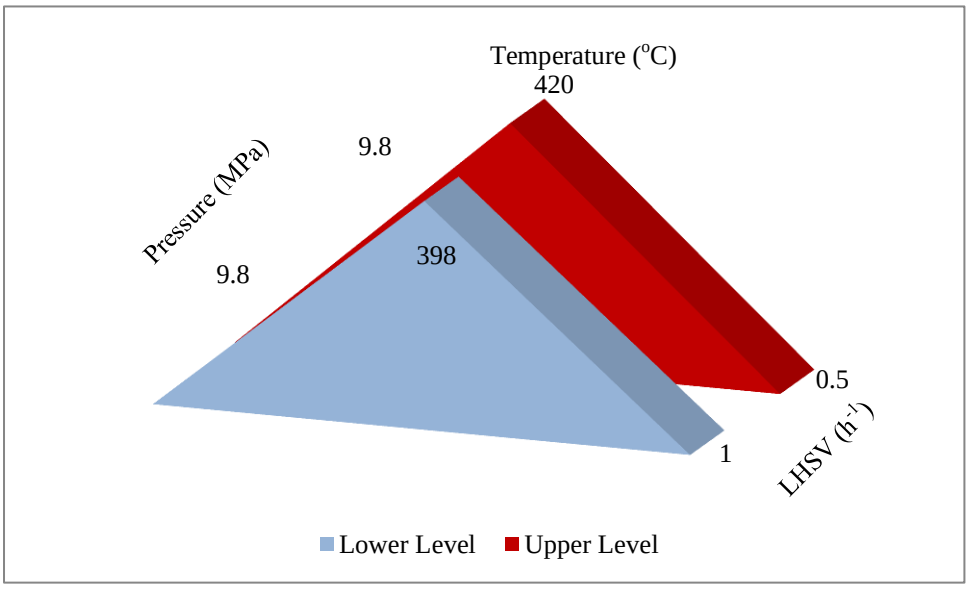

Figure 4.23: Upper and lower level of process condition

CHAPTER 5: RESULTS & DISCUSSION

5.1 Introduction

In this chapter, according to the data collected from the SOROOSH heavy oil hydro-treatment pilot (chapter 4, section 4.2), the material balance and the main properties of the upgraded samples of crude oil used are studied and the final decision for optimum process according to objective function (chapter 3 section 3.6) is then suggested.

The main products of the process consists of; naphtha, middle distillate, vacuum gas oil (VGO) and vacuum residue (VR). All properties of the feed and product samples were determined according to the ASTM standard procedures

5.2 Economic Analysis of 50,000 BPSD

The methodology used in this study follows the process in Figure 5.1. The Cost estimation in this study was based on the indigenous software which was designed during this research in Amirkabir University of Technology (AUT), named ARAMIS (Advanced Refining Applicative Model for Integrated Studies)(Jabbari & Akhavan, 2014). ARAMIS is based on a non-linear model that can simulate the main properties and main cuts of upgraded SOROOSH heavy oil. It can also estimate the capital investment required plus the operational estimation in Iran based on Advanced Barrel Curve (we discuss this latter).

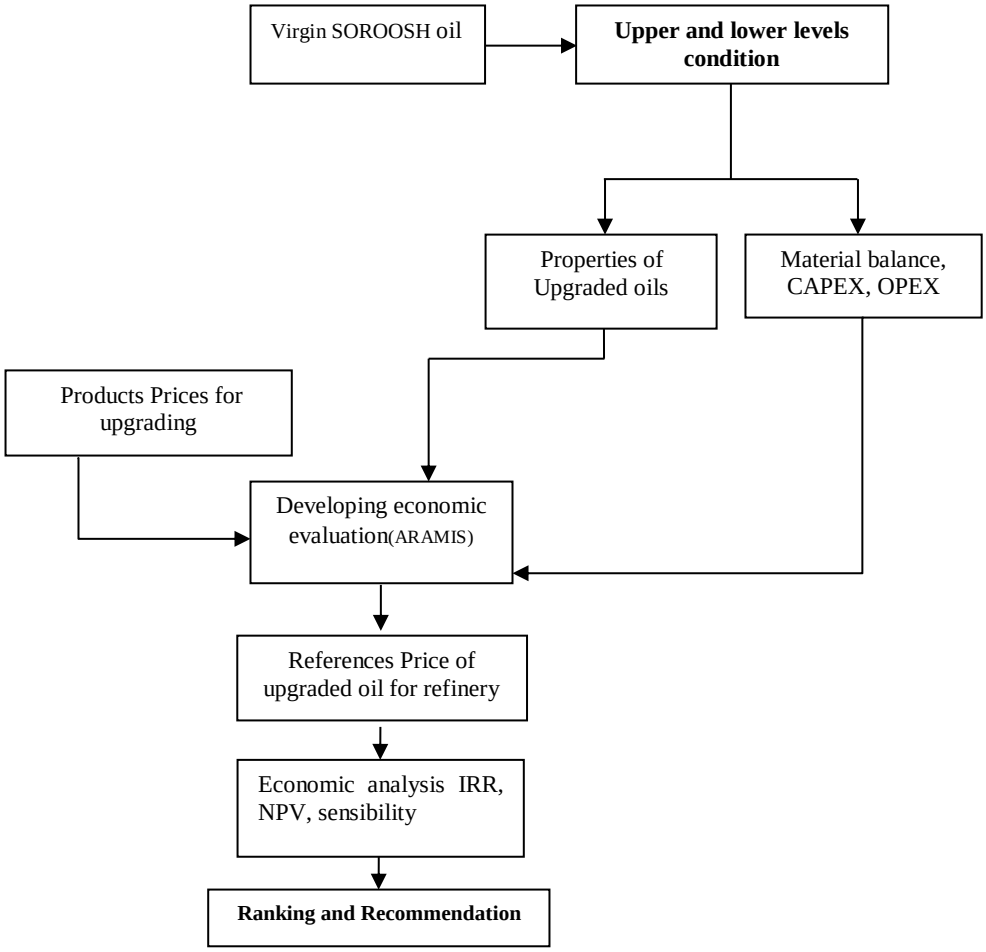

Figure 5.1: The overall economic analysis methodology in this study (Jabbari & Akhavan, 2014)

The procedure used here follows the Advanced Barrel Curve guidelines for cost estimation and the costs of major components are added to cost of the Utilities such as H_2 consumption, catalysts and energy consumptions as the main utilities in HDS process.

The level of accuracy of the direct and indirect costs estimates depend on the actual project conditions and details. With no input from the design and only choosing between various options available in the model, the model aims to deliver a Class 4 Feasibility or Pre-Design Estimate, which is prepared using cost curves and scaling factors for major processes. Cost accuracy goal is a range from -30% to +50%. (Table 5.1)

Table 5.1 :Cost estimate classification for process industries(DOE, 2011)

	Primary Characteristic		Secondary Characteristics	
ESTIMATEC LASS	**DEGREE OFPROJECTDEFIN ITION**	**END USAGE**	**METHODOL OGY**	**EXPECTEDACCURACY RANGE**
Class 5	0% to 2%	Concept screening	Capacity factored, parametric models, judgment or analogy	L: -20% to -50% H: +30% to 100%
Class 4	1% to 15%	Study or feasibility	Equipment factored or parametric models	L: -15% to -30%H: +20% to +50%
Class 3	10% to 40%	Budget authorizat ion or control	Semi-detailed unit costs with assembly level line items	L: -10% to -20% H: +10% to +30%
Class 2	30% to 70%	Control or bid/tender	Detailed unit cost with forced detailed take-off	L: -5% to -15%H: +5% to +20%
Class 1	70% to 100%	Check estimate or bid/tender	Detailed unit cost with detailed takeoff	L: -3% to -10% H: +3% to +15%

The main project assumptions are:

- Project life: 15 years
- Construction Period: 3 Years
- Prices will be evaluated based on historical prices (2011 to 2013)
- Discount rate: 10%
- Grace on Tax: None
- Depreciation for tax purposes: 10 Years
- Stream factor: 350 days
- Construction start date: 1/1/2015
- Construction period (in months): 36
- Plant start-up date: 1/1/2018

5.2.1 Capital Expenditure (CAPEX)

The cost estimates in this study, were derived based on the direct costs, indirect costs and utilities costs. These costs include the process design, engineering cost, installed costs of the process units and the cost of the facility development and infrastructure.

5.2.1.1 Direct Capital Cost (DC)

The direct cost of a component is the capital required to build that component and install it in the plant. Ideally, these costs are known from the equipment manufacturer but since most of the data is confidential, it is difficult to obtain these values for academic analyses. Therefore, in most cases, direct costs are estimated from data available in open literature.(Tables 5.2,5.3 and 5.4)

Table 5.2: Direct Cost parameters used in this study (Turton et al., 2009)

Feed Handling & Preparation
Total Installed Equipment Cost
Cooling water and other Utilities
Hydro-treatment Plant Yard
Yard Improvement
Other Infrastructure
Construction
Engineering
Working Capital
Maintenance
Education and training
Laboratories
Purchase Equipment

Table 5.3: Purchase Equipment(Turton et al., 2009)

Tanks
Recycle pump
Gas treatment stabilizer pump
Naphtha pump
Kerosene pump
Diesel pump
LPG pump
VR pump
VGO pump
Combined feed turbine pump
Hydrogen feed turbine
Naphtha stripper
Kerosene stripper
Diesel stripper
VR stripper
VGO stripper
Electric motor-drive hydrogen recycle compressor
Reactor
Crude unit
Products unit
Sour Sulphur Treating
Fence
Load Rack
Unload Rack
Generator
Fresh / Boiler Water treatment
vehicle

Table 5.4: Other Infrastructure

Instrumentation and controls
Piping
Electronic system
Building
Flare System
waste system
Fire Dept.
Admin Office
Safety Office
Control Room

5.2.1.2 Indirect Capital Cost (IC)

Besides the construction cost of each component, there are also indirect costs that need to be applied. Usually, these are applied as percentages of PFC. Indirect costs are divided into the following five categories

- General facilities capital (GFC)
- Engineering and home office overhead (EHO)
- Project contingency
- Process contingency

General facilities capital (GFC) is the capital required for the construction of general facilities like buildings, roads, shops etc. This cost is usually between 5 - 20% of PFC. Engineering and home office overhead is typically between 7 - 15% of PFC Project contingency costs are intended to factor in the uncertainty involved in the cost estimates and process contingency costs cover the uncertainty associated with the technical performance of the process. When a project is designed, all the equipment that is required is not immediately clear. Additional equipment will be necessary when the actual plant is built. To cover for this kind of uncertainty, a project contingency factor is used. The more simplified a cost estimate is, the higher the project contingency should be. When new technologies are operated, there is an uncertainty associated with its technical performance because of lack of prior experience. A process contingency factor is used to accommodate this uncertainty. The newer a technology, higher is the process contingency.

5.2.1.3 Utilities

The utility requirements for a process plant can be easily obtained from material and energy balances around the major equipment. The utilities usually include the steam, electricity, cooling water, fuels, refrigeration and fuels. The price of utilities is correlated with the price of energy (fossil fuels), so it is inherently difficult to predict.

The price of utilities in this thesis will include the price of energy; hydrogen and the cost of catalysts.

(a) ***Hydrogen Consumption***

Hydrogen consumption during hydro-processing highly is affected by the feedstock properties, impurities removal, conversion level and properties of the catalyst. The heavier feed requires substantially more addition of hydrogen to attain a fixed level of upgrading(Ancheyta & Speight, 2007).

Developing detailed mass balances in order to know not only that all streams in the process are well accounted but also the distribution of hydrogen in those streams is of vital importance to perform further studies regarding the commercial application of a new process and catalyst. The usual manner for calculating hydrogen consumption is by means of experimental data either by a hydrogen balance in gas streams or with hydrogen content in the liquid feed and products. Fig 4.23 shows all the streams involved in a general mass balance in an HDT reactor, where Gas^0 and Liq^0 are the total amounts of the gas stream entering the reactor, and liquid feedstock to be hydro-treated respectively. Gas^1 and Liq^1 are the total amount of the gas product, which contains the unreacted hydrogen, hydrogen sulfide as by-product and light hydrocarbons ranging from C_1 to C_4, and the total amount of hydro-treated liquid product respectively.

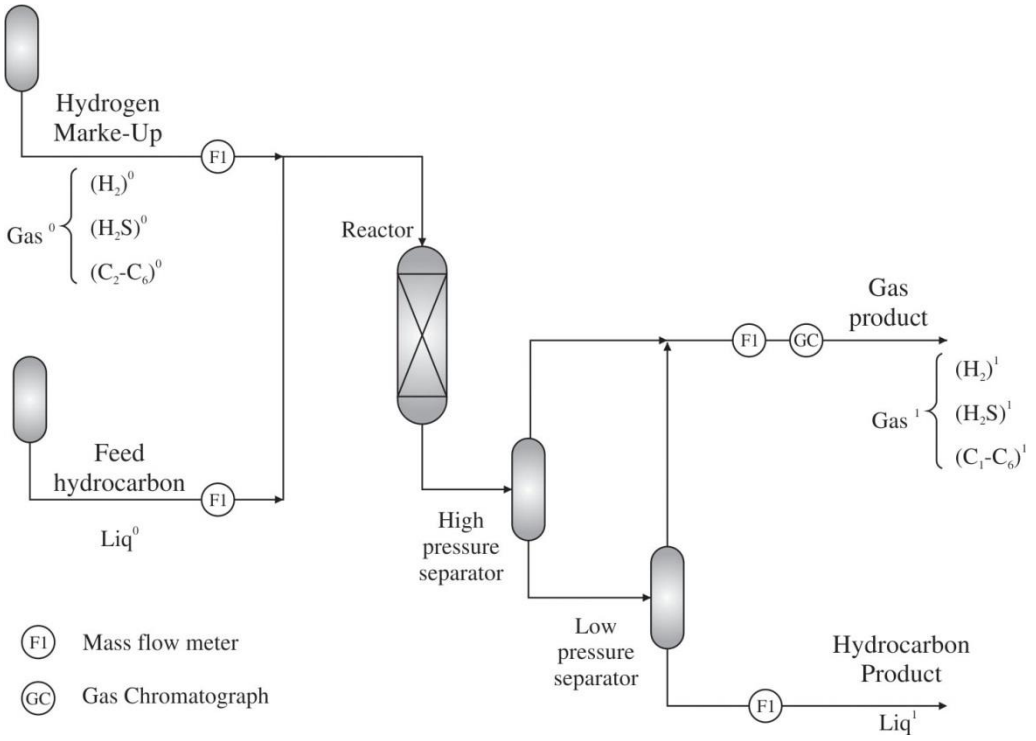

Figure 5.2: Streams involved in a mass balance of HDT process

From fig 5.2, the following mass balances can be derived:

Global balance: $Gas^0 + Liq^0 = Gas^1 + Liq^1$

Hydrogen balance in gas streams: $(H_2)^0 = (H_2)^1 + \Delta H_{gas}$

Global hydrogen balance: $H_{Gas}{}^0 + H_{Liq}{}^0 = H_{Gas}{}^1 + H_{Liq}{}^1$

Where $(H_2)^0$ and $(H_2)^1$ are the total amounts of hydrogen entering and leaving the reactor respectively. If the hydrogen purity is assumed to be close to 100%, $Gas^0 = (H_2)^0$, ΔH_{gas} is the difference between the amount of hydrogen entering and leaving the reactor determined by mass balance in the gas streams, which is commonly (and erroneously) reported as hydrogen consumption. $H_{Gas}{}^0$ and $H_{Gas}{}^1$ are the total equivalent amounts of hydrogen contained in the gas streams entering and leaving the reactor respectively which are composed by pure hydrogen, hydrogen contained in H_2S, and hydrogen contained in C_1–C_6 hydrocarbons as shown in Fig. 5.2. $H_{Liq}{}^0$ and $H_{Liq}{}^1$ are the total amounts of hydrogen contained in the liquid feedstock and in the hydro-treated

liquid product respectively. H_{Liq}^{1} includes the hydrogen content in the liquid $H_{HC\text{-}Liq}^{1}$, and the amount of hydrogen gas dissolved in the liquid H_{diss}^{1}:

$H_{Liq}^{1} = H_{HC\text{-}Liq}^{1} + H_{diss}^{1}$

The total real hydrogen consumption (H_{cons}) is thus

$H_{cons} = \Delta H_{gas} + H_{diss}^{1}$

The values of H_{Liq}^{1} and H_{Liq}^{0} are preferably obtained experimentally, e.g., by ultimate (elemental) analysis, however, they can be estimated with empirical correlations.

Based on all these equations, which are derived from mass balances, the following approaches can be established for calculating hydrogen consumption during hydro-treating operations.

I. Mass balance of hydrogen in gas stream
II. Global hydrogen balance
III. Class of hydrogen-consuming chemical reactions
IV. Hydrogen consumption by reaction average contributions
V. Hydrogen consumption by kinetic modeling

Hydrogen consumption by reaction average contributions:(Castañeda et al., 2011)

The calculation of hydrogen consumption when experimental information is not sufficient or for quick estimations can be done according to acquired experience. Edgar (1993) reported the following average contributions of each HDT reaction to the hydrogen consumption (m^3/m^3):

HDS=95–100 per each 1%wt. removed

HDN=300–350 per each 1wt% removed

HDC=25 per each 1vol. % removed

HDA=27per each 1 %wt. % removed

HDM=26 per each1 wppm removed

In addition to Edgar equations, Speight (Speight, 2007) presented a correction in hydrogen consumption by metal content (Table 5.5)

Table 5.5: Correction in hydrogen Vs. Metals content in petroleum fractions (Speight, 2007)

Ni + V (wppm)	Correction (%)	Ni + V (wppm)	Correction (%)
0-100	-2	700	12
200	1	800	16
300	2.5	900	21
400	4	1000	28
500	6.5	1100	38
600	9	1200	50

As it is known, H_2 consumption increases with the increase of pressure and temperature whereas it decreases with the increase of LHSV. Increasing the LHSV results in the decrease of hydro-treating conversions because of the reduced residence time, resulting in a decrease in H_2 consumption. H_2 consumption reaches to it's peak in accordance to the increase of temperature (Mapiour et al., 2010)

The relationship between the increasing presence of HDS% and HDM% with consuming H_2 is assumed to be exponential with respect to the degree of HSD %/HDM%, as described by the Equation (5.1):

$$H_2\left(\frac{m^3}{m^3}\right) = \alpha_1 e^{\alpha_2(HDS\%\ or\ HDM\%)} \qquad \text{Equation 5.1.}$$

The denotation of "H_2" in the equation is H_2 consumption under certain test conditions and Figures 5.3 and 5.4 show the H_2 consumption vs. temperature and HDS% respectively. In addition, figures 5.5, 5.6 and 5.7, 5.8 present the H_2 consumption vs. temperature and HDM% in HDM reactions with different values of α_1 and α_2. The values of these parameters are based on the assumption made in the Edgar (1993) report . The plots in the said figures indicate the maximum and minimum limits for α_1 and α_2.

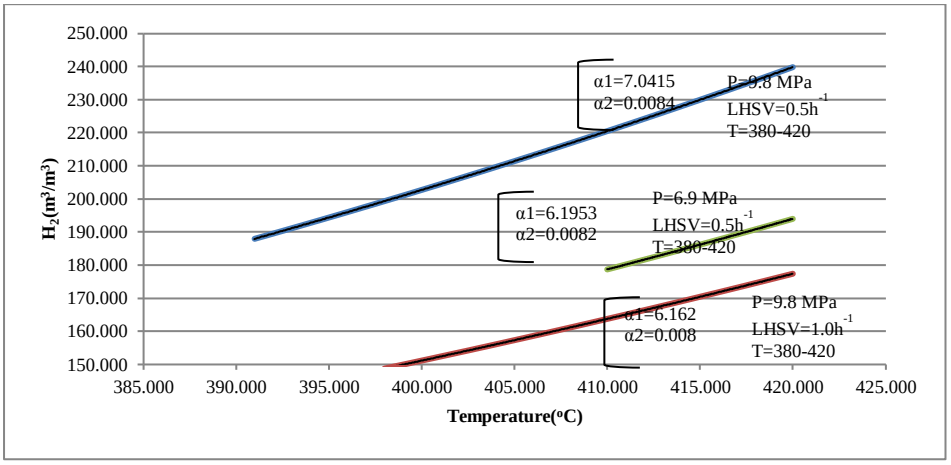

Figure 5.3: H_2 (m^3/m^3) as a function of temperature in HDS process

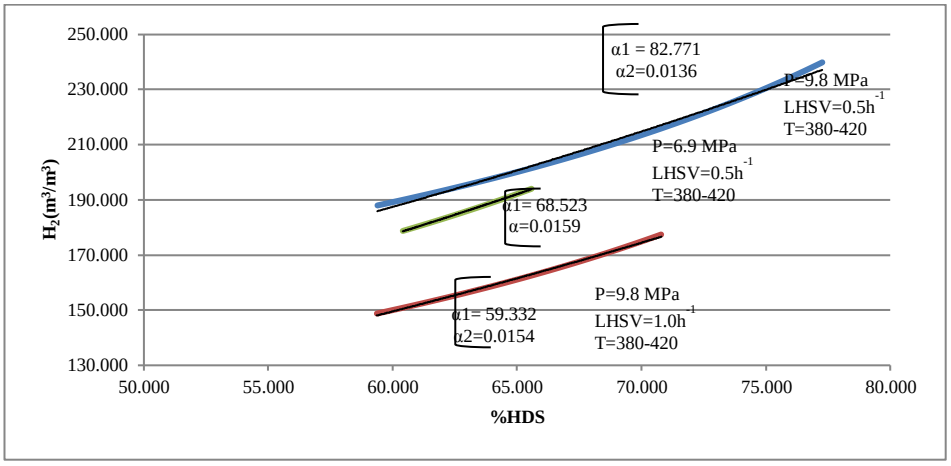

Figure 5.4: H_2(m^3/m^3)as a function of degree of %HDS

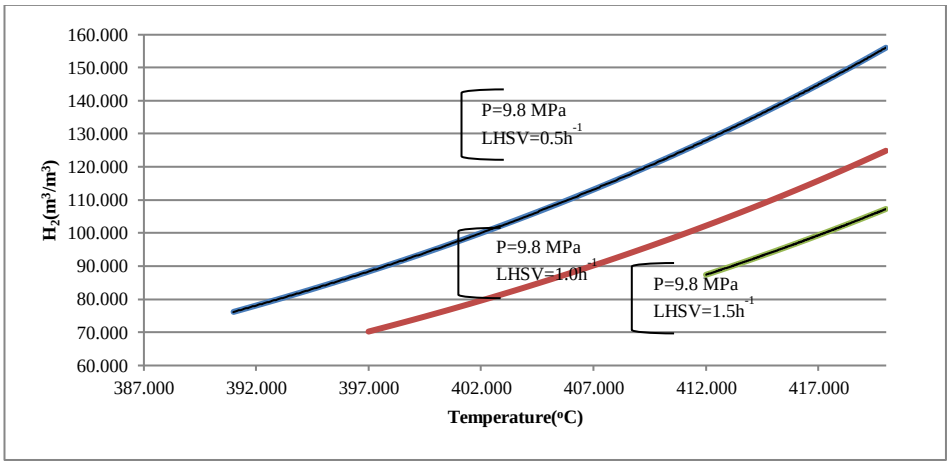

Figure 5.5: H_2 (m^3/m^3) as a function of temperature in HDM process

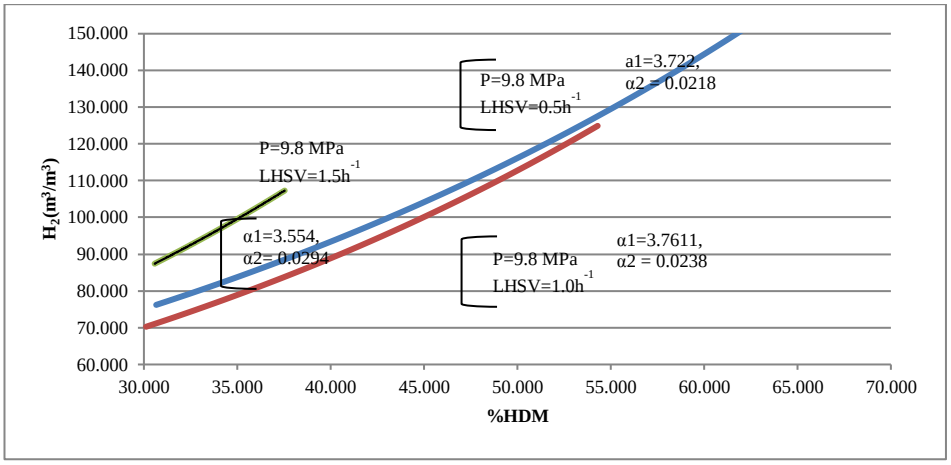

Figure 5.6: H_2 (m^3/m^3)as a function of degree of %HDM

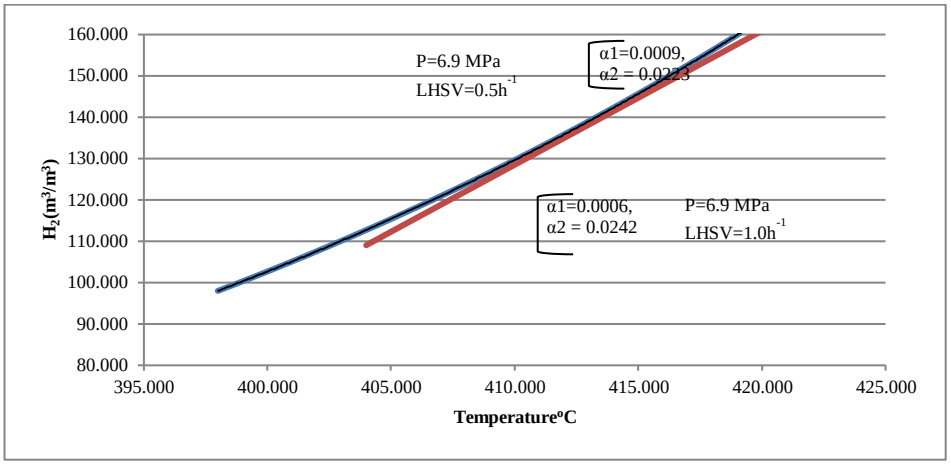

Figure 5.7: H_2 (m^3/m^3) as a function of temperature in HDM process

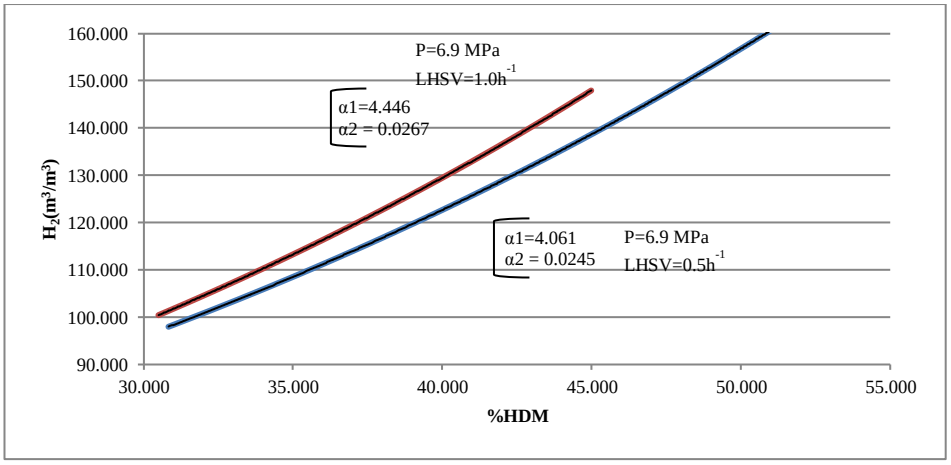

Figure 5.8: H_2 (m^3/m^3) as a function of degree of HDM%

Table 5.6 presents the $H_2(m^3/m^3)$ consumption models in different process conditions.

Table 5.6: H_2 (m^3) consumption Vs. %HDS &%HDM

Function	Conditions
$H_2 = 82.771e^{0.0136 \times HDS\%}$ **Equation 5.2**	P=9.8 MPa LHSV=0.5h^{-1} T=380-420
$H_2 = 59.332e^{0.0154 \times HDS\%}$ **Equation 5.3**	P=9.8 MPa LHSV=1.0h^{-1} T=380-420
$H_2 = 68.523e^{0.0159 \times HDS\%}$ **Equation 5.4**	P=6.9 MPa LHSV=0.5h^{-1} T=380-420
$H_2 = 3.5548e^{0.0294 \times HDM\%}$ **Equation 5.5**	P=9.8 MPa LHSV=0.5h^{-1} T=380-420
$H_2 = 3.7611e^{0.0238 \times HDM\%}$ **Equation 5.6**	P=9.8 MPa LHSV=1.0h^{-1} T=380-420
$H_2 = 3.722e^{0.0218 \times HDM\%}$ **Equation 5.7**	P=9.8 MPa LHSV=1.5h^{-1} T=380-420
$H_2 = 4.061e^{0.0245 \times HDM\%}$ **Equation 5.8**	P=6.9 MPa LHSV=0.5h^{-1} T=380-420
$H_2 = 4.446e^{0.0245 \times HDM\%}$ **Equation 5.9**	P=6.9 MPa LHSV=1.0h^{-1} T=380-420

The ANOVA test is performed to evaluate the adequacy of the models. Table 5.7 shows R^2(R-squared) and Adjusted R Square which can predict the accuracy of models for hydrogen consumption, and the results demonstrate that the regressed models fitted well.

Table 5.7: ANOVA result of the hydrogen consumption models

	R^2	Adjusted R Square
models	0.99	0.99

$$\boldsymbol{Cost\ of\ Total\ H_2 = b_{H2} \times Total\ H_2}$$ **Equation 5.10**

Where $b_{H2}$is the price hydrogen ($/m^3)

(b) ***Catalyst cost***

Temperature is the most important parameter in the hydro-treating processes and it acts as an effective tool to achieve the desired level of HDS% and HDM%. Meanwhile both HDS% and HDM% have a direct effect on catalyst deactivation and consequently on the catalyst's life. The profitability of this process depends very often on the lifetime of the catalyst. Therefore, for such processes, to achieve the desired conversion, it is vital to determine the optimum temperature and pressure. The catalyst's life is the key issue in optimizing the operation of residuum hydro-treating units. Three deactivation periods are identifiable in the catalytic hydro-processing of oil fractions: (1) Deactivation by coke, which is formed from virtually all feeds employed, and in the case of heavy oils is mainly caused from asphaltenes; (2) deactivation by metals, which is irreversible and its rate depends on the metals level in the feed; and (3) pore constriction and blockage, characterized by a very strong loss in activity, after which the plant's operation has to be stopped

Hydro-processing catalyst is mostly deactivated by coke and metals deposits. It is clear that the catalyst life is highly dependent on the degree of HDS, HDM, and their severity. The three main parameters affecting the catalyst life are; the degree of HDS/ HDM, LHSV and the temperature. These parameters were altered over the following ranges:

- Degree of HDS%/HDM% was changed from 60% to 75% for HDS and from 30% to 60% for HDM, for a feedstock with 3.9 wt.% sulphur content and 143 ppm metals.

- LHSV was altered from 0.5 to 1.5 h^{-1}, with 3 steps
- Temperature was changed from 380 to 420°C, with 10°C per steps

Modeling of catalyst deactivation during heavy oil processing is not an easy task. Different approaches to model the deactivation in different reactions have appeared in several literatures (Jiménez-García et al., 2009; Moustafa & Froment, 2003)

It is clear that the catalyst's life is highly dependent on the HDS% and HDM%. The deeper HDS%/HDM% is, the shorter the catalyst's life is. Likewise, pushing more feed through the system results in a reduced on-stream time. Figures 5.9, 5.10 and 5.11 show the catalyst's life as a function of HDS% and HDM% during the upgrading SOROOSH heavy oil respectively.

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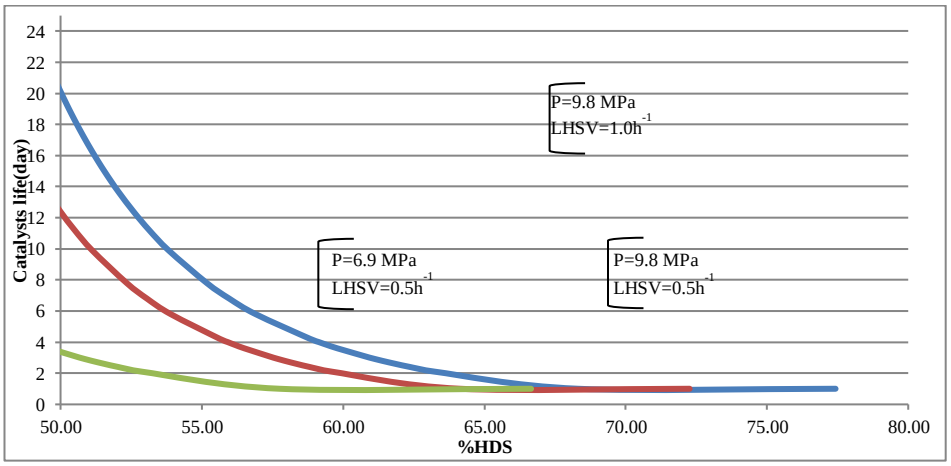

Figure 5.9: Catalysts life (day) Vs. %HDS in 380-420°C

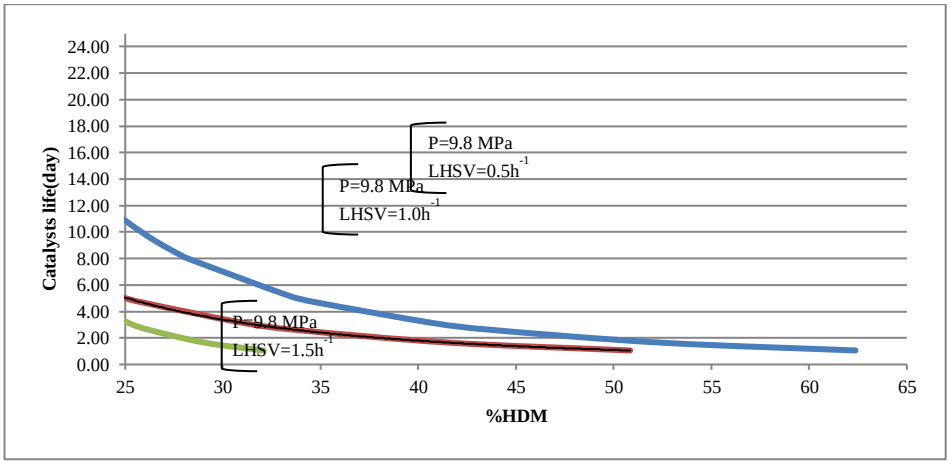

Figure 5.10:Catalysts life (day) Vs. %HDM in 380-420^{o}C

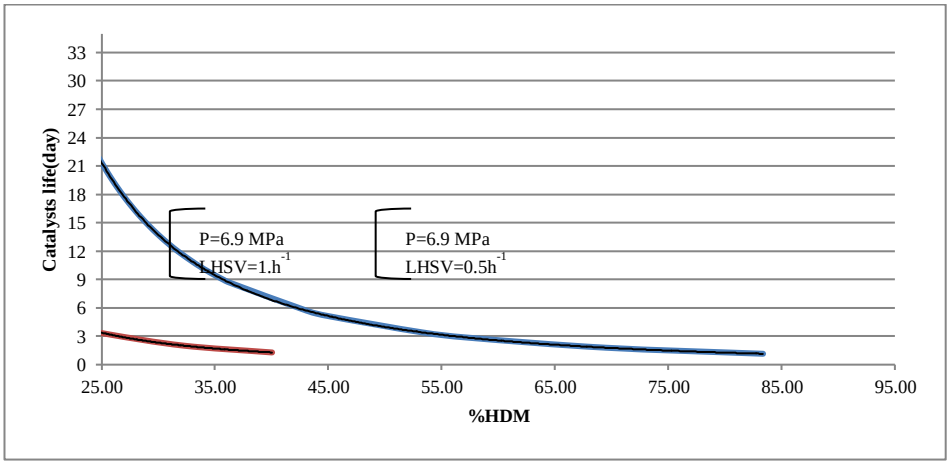

Figure 5.11: Catalysts life (day) Vs. %HDM in 380-420^{o}C

Table 5.8 shows the relation between catalysts life and %HDS /%HDM in different conditions as a power function for SOROOSH heavy oil.

Table 5.8: Catalysts life (day) Vs. %HDS &%HDM

Function		Conditions
$catalysts\ life = 1E + 16\%HDS^{-8.688}$	**Equation 5.11**	P=9.8 MPa LHSV=0.5h^{-1} T=380-420
$catalysts\ life = 4E + 16\%\ HDS^{-9.127}$	**Equation 5.12**	P=9.8 MPa LHSV=1.0h^{-1} T=380-420
$catalysts\ life = 3E + 13\ \%HDS^{-7.593}$	**Equation 5.13**	P=6.9 MPa LHSV=0.5h^{-1} T=380-420
$catalysts\ life = 39563\ \%HDM^{-2.547}$	**Equation 5.14**	P=9.8 MPa LHSV=0.5h^{-1} T=380-420
$catalysts\ life = 6051.5\ \%HDM^{-2.2.2}$	**Equation 5.15**	P=9.8 MPa LHSV=1.0h^{-1} T=380-420
$catalysts\ life = 6E + 06\%HDM^{-4.476}$ **Equation 5.16**		P=9.8 MPa LHSV=1.5h^{-1} T=380-420
$catalysts\ life = 51967\%HDM^{-2.422}$	**Equation 5.17**	P=6.9 MPa LHSV=0.5h^{-1} T=380-420
$catalysts\ life = 2409.4\ \%HDM^{-2.04}$	**Equation 5.18**	P=6.9 MPa LHSV=1.0h^{-1} T=380-420

The ANOVA test is performed to evaluate the adequacy of the models. Table 5.9 shows R^2(R-squared) and Adjusted R Square which can predict the accuracy of models for catalysts life, and the results demonstrate that the regressed models fitted well.

Table 5.9: ANOVA result of the catalysts life models

	R^2	Adjusted R Square
models	0.9717	0.96

Cost of catalysts: $C_{cat} \times Catalysts\ life_{Condition}$ Equation 5.19

(c) ***Energy Cost***

a) Cost of heat: C_{Heat} (Heat unit cost) is estimated as the cost of increasing the1ºC heat unit of the feedstock to reach the HDS/HDM. The relation between HDS % and HDM % and temperature is shown in table 5.10.

Table 5.10: Effect of increasing temperature in HDS% & HDM%

Function	Conditions
$HDS\% = 1.1264e^{0.0101\times\Delta T}$ Equation 5.20	P=9.8 MPa LHSV=0.5h^{-1}
$HDS\% = 0.5695e^{0.01114\times\Delta T}$ Equation 5.21	P=9.8 MPa LHSV=1.0h^{-1}
$HDS\% = 0.1463e^{0.0144\times\Delta T}$ Equation 5.22	P=6.9 MPa LHSV=0.5h^{-1}
$HDM\% = 0.6005e^{0.0108\times\Delta T}$ Equation 5.23	P=9.8 MPa LHSV=0.5h^{-1}
$HDM\% = 0.0007e^{0.0268\times\Delta T}$ Equation 5.24	P=9.8 MPa LHSV=1.0h^{-1}
$HDM\% = 5E-06e^{0.0379\times\Delta T}$ Equation 5.25	P=9.8 MPa LHSV=1.5h^{-1}
$HDM\% = 0.993e^{0.0146\times\Delta T}$ Equation 5.26	P=6.9 MPa LHSV=0.5h^{-1}
$HDM\% = 2E-06e^{0.0401\times\Delta T}$ Equation 5.27	P=6.9 MPa LHSV=1.0h^{-1}

$\Delta T=T_c-T_f$,T_c is the temperature required to achieve a given HDS/HDM rate and T_f is the feed set point temperature.

b) Cost of Electricity

Electrical consumption of pumps :(Table 5.11)

$$\Delta E_p = k_p \times \Delta Q_p \qquad \text{Equation 5.28}$$

Where E_P is the electrical consumption of the pump (kW); Q_P (m^3/h) is the fluid flow rate of the corresponding product and k_P is the energy coefficient. Because the specifications of the fluid do not considerably change due to the process variables, k_P can be considered to be constant.

Table 5.11: Electrical and heating equipment

Description	$k_{P,T,E}$	unit
Recycle pump	0.279	kW.h/m³
Gas treatment stabilizer pump	0.238	kW.h/m³
naphtha pump	0.749	kW.h/m³
Kerosene pump	0.488	kW.h/m³
Diesel pump	0.432	kW.h/m³
LPG pump	0.816	kW.h/m³
VR pump	0.279	kW.h/m³
VGO pump	0.279	kW.h/m³
Energy for combined feed turbine pump	238.83	KJ/m³
Energy for hydrogen feed turbine	0.686	KJ/m³
Energy for naphtha stripper	168067.23	kJ/m³
Energy for kerosene stripper	17623.7	kJ/m³
Energy for diesel stripper	17623.7	kJ/m³
Energy for VR stripper	11623.7	kJ/m³
Energy for VGO stripper	11623.7	kJ/m³

c) Fuel consumption:

I. Fuel consumption for furnace of reactor:

$$\Delta \boldsymbol{E_f} = \frac{(\Delta \boldsymbol{f_f^0} + \Delta \boldsymbol{f_R^0}) \times \boldsymbol{C_f} \times (\boldsymbol{Tb} - \boldsymbol{T_{eff}})}{\boldsymbol{3}(\boldsymbol{H_f} * \boldsymbol{Eff})} \qquad \text{Equation 5.29}$$

Where E_f is the fuel consumption for furnace(m^3/h); C_f is the heat capacity of feed (kJ/kg.°C);T_{eff} is the outlet temperature of the effluent exchanger, and *Eff* is the thermal efficiency of the furnace (0.685), *Tb* is bed temperatures of the reactor, $f_f^0$is the flow rate of fresh feed, f_R^0 is the flow rate of the recycle stream and H_f is the heating value of the local fuel gas equal to 5.327×10^4kJ/kg.(Sadighi et al., 2011)

II. Fuel consumed to produce the required steam for strippers of naphtha, kerosene and diesel, VR and VGO

$$\Delta \boldsymbol{E_E} = \frac{\boldsymbol{k_E} \times \Delta \boldsymbol{Q_E}}{\boldsymbol{H_f}} \qquad \text{Equation 5.30}$$

Where E_E is the fuel consumption of the re-boiler (m^3/h); Q_E (m^3/h) is the fluid flow rate of the naphtha, kerosene or diesel …, and k_E is the fuel coefficient. Because the

specifications of the fluid do not change considerably by the process variables, k_E can be supposed to be constant.

III. Consumed fuel to produce the required steam for the combined feed turbine pump

ii. $\Delta E_{T1} = \frac{k_T \times (\Delta f_f^0 + \Delta f_R^0)}{\rho_f \times H_f}$ Equation 5.31

Where E_{T1} is the fuel consumption of the turbine (m^3/h);$k_T$is the fuel coefficient. Because the specifications of the fluid do not change considerably by the process variables, k_T can be supposed to be constant and ρ_f is the density of feed, kg/m^3

IV. Consumed fuel to produce the required steam for the hydrogen turbine pump

$$\boldsymbol{E_{T2} = \frac{k_T \times (total\ H_2)}{\rho_H \times H_f}}$$ Equation 5.32

Where E_{T2} is the fuel consumption of the turbine (m^3/h); k_T is the pump coefficient (constant);H_2 is the hydrogen consumption in hyro-treatment reactions and ρ_H is the density of hydrogen (0.0892 kg/m^3).

$$\boldsymbol{C_{energy} = C_{heat} \times \Delta T + b_e \times \sum \Delta E_P + (b_g \times (\sum \Delta E_f + \Delta E_E + \Delta E_{T1} + \Delta E_{T2}))}$$ Equation 5.33

Where b_e and$b_g$are the prices of electricity and fuel gas respectively (Table 5.12)

Table 5.12: Price of Energy and feed in the refinery (Anonymous, 2013; Platts, 2013)

Categories	Unit	value
Catalyst Cost C_{Cat},	\$/day charge	8.8
Utility Cost (hot, cold) C_{heat}	\$J/m^3	7.5
Fuel gas	\$/m^3	88.7
Electricity	\$/kW	0.13
Hydrogen C_{H2}	\$/m^3	318
Feed (fresh SOROOSH crude oil)	\$/m^3	45

5.2.2 The main properties and main cuts of upgraded crudes

The main properties and main cuts of upgraded crudes for UL and LL conditions are presented in tables 5.13 and 5.14 (Figure 5.12) respectively:

Table 5.13: Main characteristic of upgraded oil

Priories	Process condition	Sulphur (% wt.)	Metals (wppm)	TAN (mgKOH/g)	API
Upper Level(UL)	T=420^{o}C P= 9.8 MPa LHSV=0.5 h^{-1}	0.83(78% conversion)	61.2 (57% conversion)	0.28	38.4
Lower Level(LL)	T=398^{o}C P= 9.8 MPa LHSV=1.0 h^{-1}	1.58 (60% conversion)	99 (31% conversion)	0.66	28.1

Table 5.14:Main cuts of SOROOSH upgraded crude

Main cuts	Upper Level(UL)	Lower Level(LL)
%vol Naphtha	24	16.8
%vol Kerosene+ Diesel	57.5	38.2
%vol VGO	7.2	33.1
%vol VR	11.3	11.9

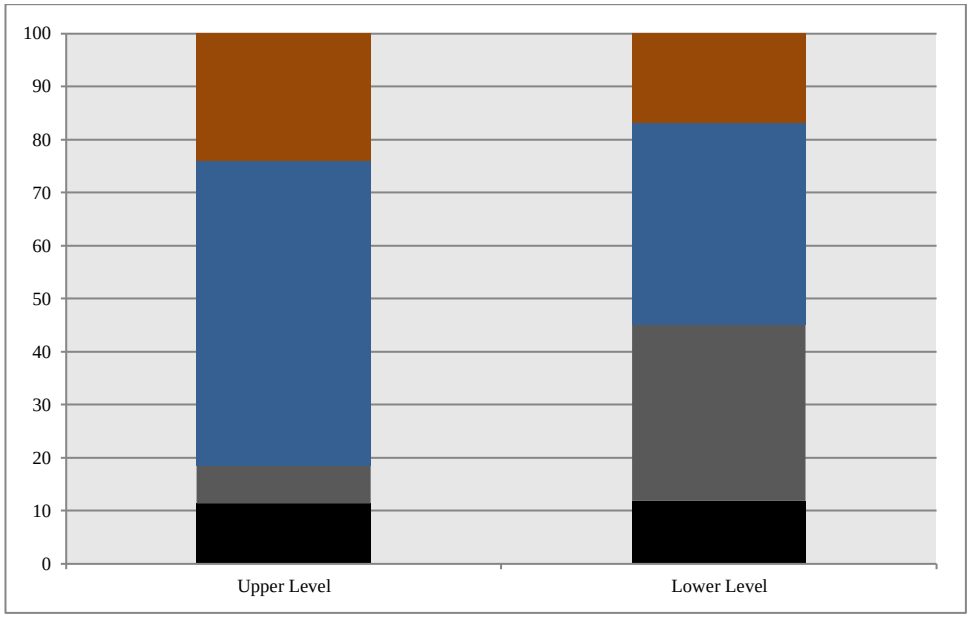

Figure 5.12: Main cuts of SOROOSH upgraded crude

The main properties of the upgraded crude in upper level and lower level are presented in tables 5.15, 5.16 and 5.17, 5.18 respectively.

Table 5.15: Main properties of the upgraded crude in Upper level

Total Upgraded Crude	
Yield/Heavy Crude	108%
°API	38.4
% S	0.83
TAN	0.28
V20°C	5.83
V50°C	2.90
V100°C	1.34
%vol Naphtha	24.0
%vol Kerosene+ Diesel	57.5
%vol VGO	7.2
%vol VR	11.3
% Fuel (380 cst)	19.0%

Table 5.16: Main properties of the upgraded crude in Upper level

Total Upgraded Crude	
Naphtha	**15-150°C**
Spgr	0.72
%S	0
TAN	0.1
Kerosene+ Diesel	**150-370°C**
Spgr	0.83
% S	0.57
TAN	0.5
Cetane Index	48
VGO	370-550°C
Spgr	0.86
%S	0
TAN	0
Vacuum Residue	**550°C+**
Spgr	1.08
% S	2.94
TAN	0
V50°C	18309557
V100°C	28388
%CCON	35.8
Ni wppm	39
V wppm	150
AsC7 %wt.	8

Table 5.17: Main properties of the upgraded crude in Lower level

Total Upgraded Crude	
Yield/Heavy Crude	102%
°API	28.1
% S	1.58
TAN	0.66
V20°C	33.99
V50°C	10.8
V100°C	3.33
%vol Naphtha	16.8%
%vol Kerosene+ Diesel	38.2%
%vol VGO	33.1%
%vol VR	11.9%
% Fuel (380 cst)	21.4%

Table 5.18: Main properties of the upgraded crude in Lower level

Total Upgraded Crude	
Naphtha	**15-150°C**
Spgr	0.71
% S	0
TAN	0.1
Kerosene+ Diesel	**150-370°C**
Spgr	0.84
% S	0.91
TAN	0.8
Cetane Index	46
VGO	**370-550°C**
Spgr	0.96
% S	2.99
TAN	1.0
Vacuum Residue	**550°C+**
Spgr	1.08
% S	2.94
TAN	0
V50°C	18309557
V100°C	28388
%CCON	35.8
Ni wppm	39
V wppm	150
AsC7 %wt.	8

5.2.3 Upgraded products prices

The prices for upgrading products are shown in table 5.19.

Table 5.19: The complete productions FOB Price ("http://www.argusmedia.com," 2012; Platts, 2013)

Categories	Unit	value
VR	$/m^3	59
VGO	$/m^3	216
Diesel	$/m^3	261
Kerosene	$/m^3	274
Light naphtha	$/m^3	273.86
Heavy naphtha	$/m^3	263.0
MTBE	$/m^3	315
LPG	$/m^3	265
Propane	$/m^3	235
Butane	$/m^3	235
Low Sulphur Fuel oil (LSFO 1.0% S)	$/m^3	144
Low Sulphur Fuel oil (HSFO 3.5% S)	$/m^3	130
Green Coke	$/m^3	26
Sulphur	$/m^3	21

For the upgraded crude the TAN should be between 0.1 and 0.8 and TAN of SOROOSH heavy crude is 0.29. The penalty for TAN should be applied for upgraded crude. For evaluation of this penalty we calculated the extra investment in metallurgy to treat a high TAN crude oil and then estimated the penalty for recovering this investment. The result is a penalty of 3.15 $/m^3 per point of TAN.

In this thesis, investment is based on the novel process, Advanced Barrel Curve, which was designed in AUT for the main upgrading process such as coker and hydro-cracking. In this process apart from the Conventional Barrel Curve, the other variables like; capacity of unit, LSHV, reactor´s outlet H_2 partial pressure, H_2 consumption, chemical consumption, coke production and …) are all taken into account and the cost estimation is carried out under the Class IV of AACE International (Association for the Advancement of Cost Estimating International) recommended practices +-20%. (Jabbari & Akhavan, 2014)

5.3 Economic comparison

5.3.1 References crude oils

Table 5.20 compares the Free Of Board (FOB) price of four references crude oils which are acceptable in our refineries (Anonymous, 2013) and the final upgraded SOROOSH price in upper level and lower level.

Table 5.20: FOB price for upgraded crude and some references (Anonymous, 2013)

Reference Crude	FOB Price ($/bbl)
URAL	107.04
BRENT	111.36
BONNY LIGHT	115.04
DAQING	108.8
SOROOSH (LL)	95.34
SOROOSH (UL)	104.44

The price of upgrading SOROOSH heavy oil in LL and UL are 95.34($/bbl.) and 104.44 ($/bbl.) respectively, it shows that the price in lower level condition is more economical in comparing to other ones.(Appendix B)

The result of the negative NPV (M$ −42,320) and smaller IRR (9.71%) than Annual Discount Rate, for upgrading 50,000 BPSD of SOROOSH heavy oil on upper level condition, make this project not attractive from an economic point of view.

The upgrading process under lower level condition, showed better results. The positive NPV (M$ 540,100) and greater the IRR (10.61%) than Annual Discount Rate, making this condition attractive from economic point of view.

5.3.2 Sensitivity analysis on natural gas price and on investment

The next step in model evaluation is to perform sensitivity analysis to identify the input parameters (and the corresponding decision variables) that are the major drivers of value creation. We simulated the aforementioned model for important parameters that affect the IRR and NPV.

Two parameters that will be analyzed here include 1) natural gas price in Iran 2) investment costs (increase and decrease by 20%).

The natural gas price is a key parameter in the hydro-treatment process because of the large hydrogen consumption during this process. The natural gas price is 88.7 $/m^3 but for Iran with large natural gas resources, this price is not so expensive. In this study the natural gas price is31 $/m^3.We first simulate the aforementioned model for 31 $/m^{3}of gas price. Table 5.21 shows the result of sensitivity analysis of upgrading SOROOSH crude oil on natural gas price. Sensitivity analyses of +/-20% on the investment are presented in table 5.22 and 5.23 respectively.

Table 5.21: Sensitivity analysis upgrading SOROOSH crude oil (Price of gas: 31 $/m^3)

	Lower level	Upper Level
Investment (M$)	1251	1631
Cash margin (M$/A)	184	241
Pay-back Time (A)	6.8	6.8
IRR %	11.8%	11.9%
NPV at 10% (M$)	178	237

Table 5.22: Sensitivity analysis upgrading SOROOSH crude oil (Investment increased by 20%)

	Lower level	Upper Level
Investment (M$)	1501	1957
Cash margin (M$/A)	164	195
Pay-back Time (A)	9.2	10.0
IRR %	8.8%	7.9%
NPV at 10% (M$)	-134	-289

Table 5.23: Sensitivity analysis upgrading SOROOSH crude oil (Investment decreased by 20%)

	Lower level	Upper Level
Investment (M$)	1001	1305
Cash margin (M$/A)	164	195
Pay-back Time (A)	6.1	6.7
IRR %	13.1%	12.0%
NPV at 10% (M$)	245	205

5.4 Summary

The economic assessment was carried out for two conditions to upgrading heavy oil process; sever condition with highest conversions in sulphur and metals and lower condition for minimum desire conversions.

The study was conducted based on hydro-treatment of 50,000 BPSD of SOROOSH heavy oil. The results reveal that, upper level condition is not economically feasible because of the high investment cost. To achieve an economic feasibility, the lower level condition, seems good scenario for project.

The capital investment factors corresponding of this study were illustrated in tables 5.2 to 5.4. The utilities were estimated based on the three main operating costs concept,

hydrogen, and energy and catalysts costs. These costs highly depend on process conditions. Table 5.19 shows the specific production costs of upgraded by products such as gasoline and diesel.

After economic analysis (Appendix C), IRR and final upgraded prices in the lower condition process and upper condition, are 10.6% 95.34($/bbl) and 9.7% 104.44 ($/bbl) respectively.

CHAPTER 6: CONCLUSION AND RECOMMENDATION

6.1 Introduction

The purpose of this Chapter is to explain specific conclusions and recommendations based on the evidence provided in previous chapters. It is hoped that, these conclusions may be useful in developing policy instruments to effect the future technological development of Iranian petroleum industries.

As we review all researches in Iran, most of them are related to hydro cracking or hydro-treatment heavy oil fractions, such as**;** atmospheric residue (AR), vacuum residue (VR) and vacuum gas oil (VGO) the direct hydro-treating of heavy crude oils has not received much attention because the refineries current situation are to the common Iranian heavy oil. However due to the decrease in these kinds of heavy oils, a switch to heavier resources with more sulphur and metals necessitate to handle them in revamped refineries. Thus in this research we explored on the upgrading process for heavier crude oil before entering to refineries in Iran

The objective of this research was to find the upgrading process condition under which a desired HDS% and HDM% conversion in the current Iranian refineries is attainable while keeping the operation expenditure as low as possible.

Therefore, an accurate and efficient objective function based on economical evaluation with technical constraints has been presented.

To find the upgrading process condition for the desired conversions, a pilot scale for the SOROOSH heavy oil hydro-treating plant, based on three main decision variables, was designed. Meanwhile the operation costs for the main three categories were modelled to demonstrate the relationships between the conversions' process and these three main cost factors.

For the commercial scale (50,000 BPSD flow rate), a full economic model (CAPEX & OPEX) was developed and applied to the analysis of the economic factors under the two operational conditions range. (Upper level & Lower level) for the hydro-treating process (i.e. temperatures, pressure and LHSV).

From the presented results and discussions, the sub objectives of this thesis are addressed as follows:

a) The models based on the relationships between temperature, pressure and LHSV and HDS% and HDM% for SOROOSH heavy oils are developed to show the importance of three hydro-treatment variables on upgrading Iranian heavy oil. The models were solved by MATLAB.
b) The models based on the relationships between the main operations cost and HDS% and HDM% for SOROOSH heavy oils are developed.
c) The comprehensive economic study for commercial upgrading process is developed

6.2 Conclusion

Based on the results obtained in this work, the following conclusions have been reached:

The experimental study was carried out for hydro-treatment of SOROOSH heavy oil under different conditions, T=380^{o}C, 400^{o}C, 420^{o}C, P=5.3 MPa, 6.9 MPa, 9.8 MPa, LHSV=0.5h^{-1}, 1.0 h^{-1}, 1.5 h^{-1} and constant H_2/Oil ratio =890 m^3/m^3. The developed models for temperature, pressure and LHSV vs. HDS% and HDM% were depicted and analyzed.

After analysis of the results, it was demonstrated that the temperature and LHSV are two factors that affect the hydro-treatment process in HDS and HDM reactions.

Subject to our refineries demand feed, (sulphur and metals less than 1.6wt% and 100wppm respectively), two margins (minimum and maximum) conditions for desired products were found.

These two conditions were named upper level and lower level.

The upper level decision variables are: T=420^{o}C, P= 9.8 MPa and LHSV=0.5 h^{-1} with a maximum conversion of sulphur and metals and the lower level condition, T=398^{o}C, P= 9.8 MPa and LHSV=1.0 h^{-1} with minimum conversions.

Also the main operation expenditures (H_2 consumption, catalysts and energy) were modelled to design the objective function.

Finally in chapter 5 the economic analysis for 50,000 BPSD of SOROOSH oil was used to find the conditions for upgrading SOROOSH heavy oil on a commercial scale. In this analysis, all capital, investment and operation costs were given as input data to ARAMIS. The IRR and NPV (for implementation of profitable upgrading process) and final price for the SOROOSH crude oil were the main output of this analysis.

The results show that the final price, IRR and NPV for upper level and lower level are 104.44 $/bbl., 9.7%,-42 and 95.34 $/bbl., 10.6%, 55 respectively. hence the lower level condition (T=398^{o}C, P=9.8 MPa and LHSV=1.0 h^{-1}) is a more beneficial condition for upgrading SOROOSH heavy oil.

6.3 Recommendations

In the following section, recommendations and suggestions for future research are presented for improvement of the upgrading of heavy oil in Iranian oil fields.

I. To use the methodology for upgrading SOROOSH products such as VR, VGO as feeds for the hydro cracking process considering different reactions i.e. de-nitrogenation and de-aromatization (hydrogenation). It is recommended that in case of performing the hydro cracking process, the Ebullated bed reactor or

series fixed bed reactors can be used for VR feed to improve the products quality.

II. For evaluation of the cost-effectiveness of the process, we can consider the export of upgraded crude oil to European and Asian Countries.

Future research could fruitfully extend the findings of the present study to other oil exporting countries.

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Jabbari, N., Akhavan, A., & Hamdi. Fuzzy Optimal models for gas reservoir management - Case of Sarajeh Gas Field (SGF). *ORAL PRESENTATION for the International Conference on Industrial Engineering and Operations Management (IEOM), Istanbul, Turkey, July 3-6, 2012*

Appendix A: ANN CODE

```
% Solve an Input-Output Fitting problem with a Neural Network
% Script generated by NFTOOL
% Created Mon Jan 12 10:49:05 SGT 2015
% This script assumes these variables are defined:
clear all
data_input=
       [380,400,420,380,400,420,380,400,420,380,400,420,380,400,420,380,400,42
       0,380,400,420,380,400,420,380,400,420;
       9.8,9.8,9.8,9.8,9.8,9.8,9.8,9.8,9.8,9.8,6.9,6.9,6.9,5.3,5.3,5.3,6.9,6.9,6.9
       ,6.9,6.9,6.9,5.3,5.3,5.3,5.3,5.3,5.3;
       0.5,0.5,0.5,1,1,1,1.5,1.5,1.5,0.5,0.5,0.5,0.5,0.5,0.5,1,1,1,1.5,1.5,1.5
       ,1,1,1,1.5,1.5,1.5];
target_sulphur=
       [1.85,1.44,0.83,2.2,1.85,1.22,2.4,2.18,1.65,2.53,2.06,1.46,2.65,2.21,1.
       68,2.73,2.37,1.85,2.85,2.59,2.19,2.83,2.47,2.01,2.97,2.74,2.4];
target_metal=[90,77.1,61.2,118.00,95.41,70.1,122.1,100.70,88.31,106.675,94.6,7
       7.90,107.95,95.823,82.710,
       131.2,113,86.2,141.4,119.91,100,133.7,117.3,93.7,141.70,127.1,105.1];
inputs = data_input;
targets = target_metal;
% Create a Fitting Network
hiddenLayerSize = 10;
net = fitnet(hiddenLayerSize);
% Choose Input and Output Pre/Post-Processing Functions
% For a list of all processing functions type: help nnprocess
net.inputs{1}.processFcns = {'removeconstantrows','mapminmax'};
net.outputs{2}.processFcns = {'removeconstantrows','mapminmax'};
% Setup Division of Data for Training, Validation, Testing
% For a list of all data division functions type: help nndivide
%net.divideFcn = 'divideind';  % Divide data randomly
[trainInd,valInd,testInd] = divideind(27,1:15,[],16:27);
%net.divideMode = 'sample';  % Divide up every sample
%net.divideParam.trainRatio = 70/100;
%net.divideParam.valRatio = 15/100;
%net.divideParam.testRatio = 15/100;
% For help on training function 'trainlm' type: help trainlm
% For a list of all training functions type: help nntrain
net.trainFcn = 'trainlm';  % Levenberg-Marquardt
% Choose a Performance Function
% For a list of all performance functions type: help nnperformance
net.performFcn = 'mse';  % Mean squared error
% Choose Plot Functions
% For a list of all plot functions type: help nnplot
net.plotFcns = {'plotperform','plottrainstate','ploterrhist', ...
  'plotregression', 'plotfit'};
% Train the Network
[net,tr] = train(net,inputs,targets);
% Test the Network
outputs = net(inputs);
errors = gsubtract(targets,outputs);
performance = perform(net,targets,outputs)
% Recalculate Training, Validation and Test Performance
%trainTargets = targets .* tr.trainMask{1};
%valTargets = targets  .* tr.valMask{1};
%testTargets = targets  .* tr.testMask{1};
%trainPerformance = perform(net,trainTargets,outputs)
%valPerformance = perform(net,valTargets,outputs)
%testPerformance = perform(net,testTargets,outputs)
% View the Network
view(net)
% Plots
% Uncomment these lines to enable various plots.
%figure, plotperform(tr)
%figure, plottrainstate(tr)
%figure, plotfit(net,inputs,targets)
%figure, plotregression(targets,outputs)
%figure, ploterrhist(errors)
```

Appendix B: GA CODE

```
[x,fval] = ga(@metal_6,1,[],[],[],[],380,420,@constraint_6);
function [c,ceq] = constraint_1( t )
%UNTITLED Summary of this function goes here
%   Detailed explanation goes here
c= [3942.8*exp(-0.02*t)-1.6; -1.6475*t + 743.87-100];
ceq= [];
end
function [ c,ceq ] = constraint_2( t )
%UNTITLED2 Summary of this function goes here
%   Detailed explanation goes here
c= [620.32*exp(-0.015*t)-1.6; -1.5285*t + 709.2-100];
ceq= [];
end
function [ c,ceq ] = constraint_3( t )
%UNTITLED3 Summary of this function goes here
%   Detailed explanation goes here
c= [ 86.961*exp(-0.009*t)-1.6; -1.2447*t + 612.07-100];
ceq= [];
end
function [ c,ceq ] = constraint_4( t )
%UNTITLED4 Summary of this function goes here
%   Detailed explanation goes here
c= [480.24*exp(-0.014*t)-1.6; -1.359*t + 639.79-100];
ceq= [];
end
function [ c ceq ] = constraint_5( t )
%UNTITLED5 Summary of this function goes here
%   Detailed explanation goes here
c=[112.01*exp(-0.01*t)-1.6; -1.295*t + 622.57-100];
ceq= [];
end
function [ c ceq ] = constraint_6( t )
%UNTITLED6 Summary of this function goes here
%   Detailed explanation goes here
c= [35.227*exp(-0.007*t)-1.6; -1.035*t + 534.44-100];
ceq= [];
end
function y = metal_1( t )
%UNTITLED11 Summary of this function goes here
%   Detailed explanation goes here
y= 100-(-1.6475*t + 743.87);
end
function y = metal_2( t )
%UNTITLED12 Summary of this function goes here
%   Detailed explanation goes here
y= 100-(-1.5285*t + 709.2);
end
function y = metal_3( t )
%UNTITLED13 Summary of this function goes here
%   Detailed explanation goes here
y= 100-(-1.2447*t + 612.07);
end
function y = metal_4( t )
%UNTITLED14 Summary of this function goes here
%   Detailed explanation goes here

y= 100-(-1.359*t + 639.79);
end
function y = metal_5( t )
%UNTITLED15 Summary of this function goes here
%   Detailed explanation goes here
y= 100-(-1.295*t + 622.57);
end
function y = metal_6( t )
%UNTITLED16 Summary of this function goes here
%   Detailed explanation goes here
y= 100-(-1.035*t + 534.44);
end
function y = sulphur_1( t )
%UNTITLED2 Summary of this function goes here
%   Detailed explanation goes here
y= 1.6 - 3942.8*exp(-0.02*t);
end
function y = sulphur_2(t)
%UNTITLED3 Summary of this function goes here
```

```
%   Detailed explanation goes here
y= 1.6-620.32*exp(-0.015*t);
end
function y = sulphur_3(t)
%UNTITLED6 Summary of this function goes here
%   Detailed explanation goes here
y= 1.6-86.961*exp(-0.009*t);
end
function y = sulphur_4( t )
%UNTITLED7 Summary of this function goes here
%   Detailed explanation goes here
y= 1.6-480.24*exp(-0.014*t);
end
function y= sulphur_5( t )
%UNTITLED9 Summary of this function goes here
%   Detailed explanation goes here
y= 1.6-112.01*exp(-0.01*t);
end
function y = sulphur_6( t )
%UNTITLED10 Summary of this function goes here
%   Detailed explanation goes here
y= 1.6-35.227*exp(-0.007*t);
end
```

Appendix C: Financial Analysis

a) Lower Level Condition

Project Summary

Private finance company, has agreed to finance $M 500,000 towards the investment at 9% over a five year period. The loan repayment schedule is as follows:

Interest Rate	Number of Installments	Year	Loan Balance	Interest Payment	Principal Payment	Total Payment	Tax Benefit of Interest
0.09	5	1	500,000	(45,000)	(83,546)	(128,546)	12,375
		2	416,454	(37,481)	(91,065)	(128,546)	10,307
		3	325,388	(29,285)	(99,261)	(128,546)	8,053
		4	226,127	(20,351)	(108,195)	(128,546)	5,597
		5	117,932	(10,614)	(117,932)	(128,546)	2,919

Financial Analysis

Proposed Project Expenditure:

Total Capital Costs	1,650,000	(1)
Total Other cost	65,000	
Total Investment	1,715,000	
Financed through Bank	(500,000)	
Net Cash Outlay	1,215,000	
Project Analysis Required?	Yes	

(1): $M 650,000 of this price is subject to capitalization. Depreciation deducted on the tax return differs from depreciation for accounting purposes:

Year	Tax Return Depreciation	Accounting Depreciation	Tax Benefit Depreciation
1	325,000	65,000	89,375
2	162,500	65,000	44,688
3	81,250	65,000	22,344
4	40,625	65,000	11,172
5	40,625	65,000	11,172
6		65,000	
7		65,000	
8		65,000	
9		65,000	
10		65,000	
Total	650,000	650,000	

Cash Flow Analysis

Year	Revenues	Operation costs	Other Costs	Depreciation Deduction	Taxable Income
1	535,800	(112,000)	(38,000)	(325,000)	60,800
2	585,900	(155,100)	(46,500)	(162,500)	221,800
3	612,600	(188,600)	(54,100)	(81,250)	288,650
4	636,050	(202,900)	(63,200)	(40,625)	329,325
5	644,112	(224,200)	(68,900)	(40,625)	310,387
6	653,500	(241,600)	(72,110)		339,790
7	668,200	(258,800)	(77,800)		331,600
8	677,400	(272,100)	(83,100)		322,200
9	689,800	(287,800)	(88,900)		313,100
10	705,300	(298,400)	(94,200)		312,700
11	712,900	(309,100)	(97,800)		306,000
12	719,600	(319,400)	(101,050)		299,150
13	722,800	(325,400)	(104,900)		292,500
14	729,100	(329,900)	(107,800)		291,400
15	734,300	(334,100)	(110,100)		290,100

Less Taxes	Net Income	Add Back Depreciation	Working Capital	Cash Flow
(16,720)	44,080	325,000	(29,500)	339,580
(60,995)	160,805	162,500	(33,100)	290,205
(79,379)	209,271	81,250	(35,600)	254,921
(90,564)	238,761	40,625	(37,900)	241,486
(85,356)	225,031	40,625	(38,400)	227,256
(93,442)	246,348		(39,200)	207,148
(91,190)	240,410		(40,400)	200,010
(88,605)	233,595		(41,200)	192,395
(86,103)	226,998		(41,900)	185,098
(85,993)	226,708		(42,300)	184,408
(84,150)	221,850		(42,800)	179,050
(82,266)	216,884		(43,600)	173,284
(80,438)	212,063		(44,100)	167,963
(80,135)	211,265		(44,600)	166,665
(79,778)	210,323		(45,100)	165,223

Economic Analysis

Year	Cash Flow	Present Value
0	(1,215,000)	(1,215,000)
1	339,580	308,709
2	290,205	239,839
3	254,921	191,526
4	241,486	164,938
5	227,256	141,108
6	207,148	116,930
7	200,010	102,637
8	192,395	89,754
9	185,098	78,499
10	184,408	71,097
11	179,050	62,756
12	173,284	55,214
13	167,963	48,653
14	166,665	43,888
15	165,223	39,553
Net Present Value		540,100

Required Rate of Return for Project => 10.00%

Net Present Value $M 540,100
IRR 10.61%

b) Upper Level Condition

Project Summary

Private finance company, has agreed to finance $M 500,000 towards the investment at 9% over a five year period. The loan repayment schedule is as follows:

Interest Rate	Number of Installments	Year	Loan Balance	Interest Payment	Principal Payment	Total Payment	Tax Benefit of Interest
0.09	5	1	500,000	(45,000)	(83,546)	(128,546)	12,375
		2	416,454	(37,481)	(91,065)	(128,546)	10,307
		3	325,388	(29,285)	(99,261)	(128,546)	8,053
		4	226,127	(20,351)	(108,195)	(128,546)	5,597
		5	117,932	(10,614)	(117,932)	(128,546)	2,919

Financial Analysis

Proposed Project Expenditure:

Total Capital Costs	2,066,000	(1)
Total Other cost	65,000	
Total Investment	2,131,000	
Financed through Bank	(500,000)	
Net Cash Outlay	1,631,000	
Project Analysis Required?	Yes	

(1): $M 650,000 of this price is subject to capitalization. Depreciation deducted on the tax return differs from depreciation for accounting purposes:

Year	Tax Return Depreciation	Accounting Depreciation	Tax Benefit Depreciation
1	325,000	65,000	89,375
2	162,500	65,000	44,688
3	81,250	65,000	22,344
4	40,625	65,000	11,172
5	40,625	65,000	11,172
6		65,000	
7		65,000	
8		65,000	
9		65,000	
10		65,000	
Total	650,000	650,000	

Cash Flow Analysis

Year	Revenues	Operation costs	Other Costs	Depreciation Deduction	Taxable Income
1	589,380	(161,767)	(68,000)	(325,000)	34,614
2	644,490	(211,668)	(35,000)	(162,500)	235,322
3	673,860	(257,489)	(54,100)	(81,250)	281,021
4	699,655	(296,746)	(63,200)	(40,625)	299,084
5	708,523	(325,680)	(68,900)	(40,625)	273,318
6	718,850	(344,833)	(72,110)		301,907
7	735,020	(368,110)	(77,800)		289,110
8	745,140	(385,010)	(83,100)		277,030
9	758,780	(399,229)	(88,900)		270,651
10	775,830	(426,030)	(94,200)		255,600
11	784,190	(436,929)	(97,800)		249,461
12	791,560	(441,301)	(101,050)		249,209
13	795,080	(447,457)	(104,900)		242,723
14	802,010	(452,106)	(107,800)		242,104
15	807,730	(471,011)	(110,100)		226,619

Less Taxes	Net Income	Add Back Depreciation	Working Capital	Cash Flow
(9,519)	25,095	325,000	(29,500)	(1,631,000)
(64,714)	170,608	162,500	(33,100)	330,000
(77,281)	203,740	81,250	(35,600)	300,000
(82,248)	216,836	40,625	(37,900)	250,000
(75,162)	198,155	40,625	(38,400)	220,000
(83,024)	218,883		(39,200)	200,000
(79,505)	209,605		(40,400)	180,000
(76,183)	200,847		(41,200)	170,000
(74,429)	196,222		(41,900)	160,000
(70,290)	185,310		(42,300)	155,000
(68,602)	180,859		(42,800)	143,866
(68,533)	180,677		(43,600)	138,508
(66,749)	175,974		(44,100)	137,742
(66,579)	175,525		(44,600)	132,421
(62,320)	164,299		(45,100)	130,123

Economic Analysis

Year	Cash Flow	Present Value
0	(1,631,000)	(1,631,000)
1	330,000	300,000
2	300,000	247,934
3	250,000	187,829
4	220,000	150,263
5	200,000	124,184
6	180,000	101,605
7	170,000	87,237
8	160,000	74,641
9	155,000	65,735
10	143,866	55,466
11	138,508	48,546
12	137,742	43,889
13	132,421	38,358
14	130,123	34,265
15	(1,631,000)	28,727
Net Present Value		-42,320

Required Rate of Return for Project => 10.00%

Net Present Value $M -42,320
IRR 9.71%